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Review

Review of volatile organic compound source apportionment by chemical mass balance

John G. Watson*, Judith C. Chow, Eric M. Fujita

Desert Research Institute, 2215 Raggio Parkway, Reno, NV 89512, USA

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Abstract

The chemical mass balance (CMB) receptor model has apportioned volatile organic compounds (VOCs) in more than 20 urban areas, mostly in the United States. These applications differ in terms of the total fraction apportioned, the calculation method, the chemical compounds used in the calculation, the apportionment units, and the source profiles applied. Nevertheless, they show similar results for VOC fractions contributed by different sources. Gasoline vehicle exhaust, liquid gasoline, and gasoline evaporation contribute up to 50% or more of the ambient VOCs in many of these studies. Relative motor vehicle source contributions determined by CMB were similar to or larger than their proportions in emissions inventories. Coatings and solvent contributions from CMB were much lower than the proportions attributed to these sources in current emissions inventories. Several measurement and reporting conventions would facilitate CMB analyses of VOC data sets.

Keywords: Receptor model; Volatile organic compounds; Ozone; Emissions; Source profiles; Emissions inventory; NARSTO

1. Introduction

Reactive organic gases (ROG) are essential to the formation of excessive tropospheric ozone in urban areas (Calvert, 1976; Seinfeld and Pandis, 1997). Organic radicals produced by the oxidation of organic gases react with nitrogen oxide to form nitrogen dioxide, thereby shifting the photostationary equilibrium between ozone and nitrogen oxide and allowing ozone to accumulate. Though meteorological conditions and transport are also important variables for ozone accumulation, only nitrogen oxides (NO_x) and ROG can be manipulated by humans, and they are the primary focus of emissions reduction programs. Most oxides of nitrogen are emitted by combustion sources and can be continuously measured with good accuracy and precision at source and receptor. ROG, on the other hand, consist of hundreds of separate compounds originating from many different sources, both anthropogenic and natural. Measurement methods are imperfect and cumbersome.

Although most ROG emissions studies have been related to ozone, the recent National Ambient Air Quality Standards (NAAQS, U.S. EPA, 1997a) for $PM_{2.5}$ (particles with aerodynamic diameters less than 2.5 μm) enhance interest in the role played by different ROG in the formation of secondary organic aerosol and nitric acid (that turns into particle nitrate when combined with ammonia). Secondary organic compounds in particulate matter include aliphatic acids, alcohols, aromatic acids, nitro-aromatics, carbonyls, esters, phenols, and aliphatic nitrates (Bowman et al., 1995; Grosjean, 1992; Pandis et al., 1992; Seinfeld and Pandis, 1997). The exact precursors of these secondary organics are not well understood, but they are generally assumed to be heavier hydrocarbons (i.e., molecules that contain more than seven or eight carbon atoms).

Odum et al. (1997) identify aromatics as the major group of commonly measured ROG that affect both ozone and secondary aerosol formation. Meng et al. (1997) demonstrate how changes in ROG emissions in

* Corresponding author. Tel.: +1-775-674-7046; fax: +1-775-674-7009.

E-mail address: johnw@dri.edu (J.G. Watson).

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Los Angeles that reduce ozone concentrations may inadvertently increase $PM_{2.5}$ concentrations, and vice versa. Many ROG compounds have also been identified as toxic substances, and substantial effort has been placed in characterizing their sources (e.g., Edgerton and Czuczwa, 1989; Harley and Cass, 1994). Volatile organic compounds (VOCs) are found indoors as well as outdoors (Lewis and Zweidinger, 1992). Though not important to tropospheric pollution, halocarbons have been used as refrigerants, degreasers, and fire suppressants, and participate in the reduction of stratospheric ozone. Halocarbons have also been used in receptor models to determine contributions to other pollutants from distant sources (Bastable et al., 1990).

This review examines how the chemical mass balance (CMB) receptor model has been applied to quantify ambient VOC source contributions to ambient concentrations of organic gases, especially those that have been identified as ozone precursors. It explains how CMB source contribution estimates are used to evaluate and improve ROG emissions inventories for ozone models. In the process of this review, several deficiencies and inconsistencies in source composition data bases, source and receptor measurement strategies, and data reporting conventions are identified. Recommendations for standardized approaches are given. It is proposed that the CMB could also be used to evaluate the output of complex, source-oriented air quality models, and that model outputs should be adapted to accommodate this application.

2. Definitions

Several terms are used inconsistently but interchangeably to describe different fractions of atmospheric organic material. Common definitions and units must be used for ambient concentrations, source profiles, and emissions rates. The following terms reflect current usage, which is frequently ambiguous:

- *Reactive organic gases* (*ROG*): Organic gases with potential to react (<30 day half-life) with the hydroxyl radical and other chemicals, resulting in ozone and secondary organic aerosol. The most reactive chemicals are not necessarily the largest contributors to undesirable end products, however, as this depends on the magnitude of their emissions as well as on their reactivity (Carter and Lurmann, 1991).
- *Total organic gases* (*TOG*): Organic gases with and without high hydroxyl reactivity. TOG typically includes ROG plus methane and halocarbons.
- *PAMS target hydrocarbons*: Fifty-five target hydrocarbons and non-methane organic compounds (NMOC) measured at photochemical assessment monitoring stations (PAMS). NMOC is operationally defined as the sum of hydrocarbons up to n-undecane.
- *Non-methane hydrocarbons (NMHC, also termed "light" hydrocarbons)*: C_2–C_{12} (light) hydrocarbons collected in stainless-steel canisters and measured by gas chromatography with flame ionization detection (GC-FID) by EPA method TO-14 (U.S. EPA, 1997b). NMHC excludes carbonyl compounds, halocarbons, carbon dioxide, and carbon monoxide even though some of these may be quantified by the same method. NMHC is most often used to quantify ozone precursors.
- *Heavy hydrocarbons*: C_{10}–C_{20} hydrocarbons collected on Tenax absorbing substrates and analyzed by thermal desorption and gas chromatography (Pellizzari et al., 1984; Zielinska and Fujita, 1994a; Clausen and Wolkoff, 1997). These are sometimes termed "semi-volatile" compounds because the $>C_{15}$ compounds are often found as both gases and particles. Most of the total hydrocarbon mass is measured in the gas phase.
- *Carbonyl compounds*: Aldehydes and ketones, the most common being formaldehyde, acetone, and acetylaldehyde (Altshuller, 1993). Carbonyls are operationally defined as C_1–C_7 oxygenated compounds measured by collection on acidified 2,4-dinitrophenylhydrazine (DNPH)-impregnated C_{18} cartridges and analyzed by high-performance liquid chromatography with UV detection (HPLC/UV) (Zielinska and Fujita, 1994b; Kleindienst et al., 1998).
- *Non-methane organic gases* (*NMOG*): NMHC plus carbonyls.
- *Semi-volatile organic compounds* (*SVOC*): Particles and gases collected on filters backed with solid absorbent such as polyurethane foam (PUF) and XAD, extracted in a variety of solvents, and analyzed by gas chromatography/mass spectrometry or HPLC/UV (Chuang et al., 1987). This class includes compounds such as polycyclic aromatic hydrocarbons (PAHs), methoxyphenols and lactones, pesticides, and other polar and non–polar organic compounds. The heavy hydrocarbons are often classified as SVOCs, but they are given a separate identity here for precision and clarity.
- *Volatile organic compounds* (*VOCs*): NMHC plus heavy hydrocarbons plus carbonyls plus halocarbons, typically $<C_{20}$. VOC has been imprecisely used to describe most of the other categories described above.

Subsets of VOC compounds have been used to distinguish among sources in CMB analyses. Most of these compounds are also precursors or end products for chemical reactions that create ozone, suspended particles, and deplete stratospheric ozone. These compounds are most often quantified and reported by VOC analyses, even though many other peaks are often found in a chromatogram. These unidentified peaks are normally converted into a presumed mass and summed into an "unidentified" fraction. The selection of "identified" and "unidentified" peaks is not standardized, thereby

limiting comparability of this fraction among different laboratories.

Non-standard variable definitions and units are an impediment to VOC source apportionment using the CMB. VOC concentrations are usually reported in ppbC or $\mu g\,m^{-3}$ at local temperature and pressure. Either unit is acceptable for CMB analysis, but the units used to calculate source profile ratios must be consistent with those of the ambient measurements.

3. Chemical mass balance receptor model

The CMB receptor model (Friedlander, 1973; Watson, 1984; Watson et al., 1984, 1990, 1998) consists of a least-squares solution to a set of mass-balance equations that express each receptor chemical concentration as a linear sum of products of source profile abundances and source contributions. The source profile abundances (i.e., the mass fraction of a chemical or other property in the emissions from each source type) and the receptor concentrations, with appropriate uncertainty estimates, serve as CMB input data. CMB calculates values for the contributions from each source type and the uncertainties of those values.

3.1. CMB procedures

The CMB modeling procedure requires (1) identification of the contributing sources types; (2) selection of chemical species or other properties to be included in the calculation; (3) estimation of the fraction of each of the chemical species which is contained in each source type (source profiles); (4) estimation of the uncertainty in both ambient concentrations and source profiles; and (5) solution of the CMB equations.

The effective variance weighted solution to the CMB model (Watson et al., 1984) is almost universally applied because it (1) yields an approximately unbiased solution to the CMB equations, providing model assumptions are met; (2) uses all available chemical measurements, not just "tracer" species; (3) estimates the uncertainty of the source contributions based on precisions of both the ambient concentrations and source profiles; and (4) gives chemical species with higher precisions in both the source and receptor measurements greater influence than species with lower precisions.

3.2. CMB assumptions and testing

CMB model assumptions are (1) compositions of source emissions are constant over the period of ambient and source sampling; (2) chemical species do not react with each other (i.e., they add linearly); (3) all sources with a potential for significantly contributing to the receptor have been identified and have had their emissions characterized; (4) the number of sources or source categories is less than or equal to the number of species; (5) the source profiles are sufficiently different from one another; and (6) measurement uncertainties are random, uncorrelated, and normally distributed. The degree to which these assumptions are met in applications depends to a large extent on the particle and gas properties that are measured at source and receptor.

CMB model performance is examined generically, by applying statistical tests such as collinearity and influence diagnostics (Kim and Henry, 1989; Henry, 1992) and randomized testing methods (e.g., Monte Carlo simulations with synthetic data sets, Javitz et al., 1988) to determine the feasibility of using specific source profiles to resolve source contributions by CMB, and specifically for each application by following an applications and validation protocol. When source profiles are similar, or collinear, their CMB source contribution estimates have large uncertainties. CMB can tolerate reasonable deviations from the CMB model assumptions, though these deviations contribute to errors in the estimated source contributions that may exceed the calculated uncertainties (deCesar and Cooper, 1982; Henry, 1992; Currie et al., 1984; Dzubay et al., 1984; Lowenthal et al., 1992; Javitz et al., 1988).

A CMB model application and validation protocol (U.S. EPA, 1987; Watson et al., 1998) is followed to apportion gaseous and particle organic compounds (Fujita et al., 1994; Watson et al., 1994). This protocol (1) determines model applicability; (2) selects a variety of profiles to represent identified contributors; (3) evaluates model outputs and performance measures; (4) identifies and evaluates deviations from model assumptions; (5) identifies and corrects input data deficiencies; (6) verifies consistency and stability of source contribution estimates; and (7) evaluates CMB results with respect to other data analysis and source assessment methods.

3.3. CMB limitations

CMB complements rather than replaces other data analysis and modeling methods. CMB helps explain observations that have already been taken, but it is not predictive. When source contributions are proportional to emissions, as they often are for VOCs, then a source-specific proportional rollback (Chang and Weinstock, 1975) is used to estimate the effects of emissions reductions. Similarly, when a secondary compound apportioned by CMB is known to be limited by a certain precursor, a proportional rollback is used on the controlling precursor.

CMB does not explicitly treat profiles that change between source and receptor. Atmospheric lifetimes for many VOCs can be short, especially when photochemical activity is intense (Atkinson, 1990; Carter and Lurmann, 1991). Emissions measurements in point-source stacks

employ dilution to ambient temperatures and < 1 min of residence time prior to collection to allow for condensation and rapid transformation. Conversely, tunnel studies allow for aging of vehicle emissions before sampling. Profiles have been "aged" prior to submission to CMB using aerosol and gas chemistry models to simulate changes between source and receptor and to estimate specific VOC source impacts on ozone concentrations (Chung et al., 1996; Lin and Milford, 1994). These models require additional assumptions regarding chemical mechanisms, relative transformation and deposition rates, mixing volumes, and transport times; these assumptions must be stated and evaluated as part of a CMB application.

4. VOC source compositions and profiles

Emissions inventories typically show stationary sources and on-road mobile sources contributing equally to total ROG emissions in an area. Fujita et al. (1997a) compared emissions inventories from the entire state of Massachusetts with those from California's South Coast Air Basin (SoCAB) and found, respectively, for each area: (1) 45% (SoCAB) and 46% (Mass.) of ROG from stationary emitters such as fuel combustion, waste burning, solvent use, petroleum processing storage and transfer, industrial processing, and miscellaneous processes; (2) 46 and 34% from on-road vehicles, including spark ignition and diesel; and (3) 9 and 21% from off-road vehicles, including trains, ships, aircraft, and construction/agricultural equipment. Solvent use, including industrial and architectural coatings, is the largest component of stationary sources, constituting 29% (Los Angeles) and 38% (Mass.) of the total ROG inventory. Biogenic emissions are not normally quantified as part of urban inventories unless a special study is conducted.

The emissions inventory is the starting point for a CMB source apportionment to identify potential contributors to ambient concentrations. Vehicle-related emissions, including exhaust, evaporated fuel, and even liquid fuel are ubiquitous in all urban areas and are always included. Architectural (i.e., paints) and industrial solvents (i.e., cleaning and process solvents, as in printing) are also common to, but highly variable in, most urban areas. Petrochemical production and oil refining are more specific to certain urban settings, such as the Texas coast, where these activities are numerous. Biogenic emissions are larger in the eastern US, where forests are lush, in contrast to the arid west. ROG emissions in inventories are often reported in equivalent units of methane or propane. Comparisons of relative CMB source attributions to emissions inventories require appropriate reconciliation between the inventory units and source contribution units (Kenski et al., 1995).

Source profiles are needed from representatives of these source types to apply the CMB and to translate ROG inventories into speciated inventories for air quality models. Several compilations or "libraries" of VOC source profiles have been assembled (Shareef et al., 1988; Scheff et al., 1989; Doskey et al., 1992; Harley et al., 1992; Fujita et al., 1997a) from original measurements and a combination of published and unpublished test results. Most of these profiles are limited for CMB use because (1) they represent older technology and fuels that are different today; (2) documentation is lacking or insufficient; (3) compound abundances are normalized to different definitions of NMOG or NMHC and are derived from a variety of measurement units; and (4) reported VOCs are not the same among profiles.

Fractional abundances have been determined by dividing VOCs measured in source samples, reported in ppbC or $\mu g\ m^{-3}$ by (1) NMHC, as described above, including the unidentified fraction; (2) the sum of the quantified or most abundant compounds, which varies depending on the investigator; (3) the sum of all canister measurements, including non-reactive gases such as halocarbons; and (4) NMOG, the sum of all VOCs measured from all applied methods. The profile differences make it difficult in practice to compare and use profiles from different studies. Furthermore, inventories employ different conventions for defining VOC. Comparison of CMB results with inventories requires a common reference. Since the TO-14 method is applied to PAMS (Lewis et al., 1998) at all severe ozone non-attainment areas, it is recommended that the sum of the 55 PAMS target hydrocarbons should be the common normalization standard for source profiles. Measurements from other canister analyses, Tenax, and DNPH should also be normalized to the sum of the PAMS species. With this common convention, renormalization to NMOG or other categories is straightforward. Table 1 identifies the PAMS species and shows examples of source profiles normalized to their sum.

The largest body of knowledge about organic gas source compositions is related to mobile source emissions (Black et al., 1980; Zweidinger et al., 1988; Williams et al., 1990; Wallington et al., 1993; Haszpra and Szilagyi, 1994; Pierson et al., 1996; Sagebiel et al., 1996; Fujita et al., 1997a, b; Gertler et al., 1996; Mugica et al., 1998; Siegl et al., 1999). These tests include emissions from spark-ignition (gasoline-fueled) vehicle exhaust, compression-ignition (diesel-fueled) vehicle exhaust, liquid gasoline, and evaporative gasoline emissions from fuel handling and vehicle operation.

The examples in the first four columns of Table 1 demonstrate the similarities and differences between vehicle exhaust, liquid gasoline, and evaporated gasoline profiles. With only the light hydrocarbons measured, the heavy-duty diesel and light-duty gasoline exhaust profiles are similar, and are often collinear in CMB

calculations. Ethene, acetylene, 1-butene, iso-butene, propane, propene, isopentane, n-pentane, 2,2-dimethylbutane, 2-methylpentane, n-hexane, benzene, 3-methyhexane, toluene, ethylbenzene, *m*- and *p*-xylene, *m*-ethyltoluene, and 1,2,4-trimethylbenzene, are the most abundant compounds in either or both of these emissions. Several of these are short lived, and are only used in CMB calculations where fresh emissions are expected, as during early morning. Major differences between these two exhaust profiles are evident for (1) acetylene, iso-butene, isopentane, n-hexane, and 2-methylhexane that are most abundant in gasoline exhaust; and (2) for propene, propane, 2,2-dimethylbutane, n-decane, and n-undecane that are more abundant in diesel exhaust. Gertler et al. (1996) show that the CMB discrimination between diesel and gasoline exhaust is distinctive when the heavy hydrocarbons are included. Most of these compounds are highly enriched in diesel exhaust but have negligible abundances in normal-running gasoline vehicle exhaust.

Liquid gasoline contains many compounds in common with gasoline vehicle exhaust. It is depleted in combustion products such as ethane, ethene, and acetylene. Evaporated gasoline is also depleted in these combustion compounds, as well as heavier hydrocarbons that volatilize more slowly from liquid fuels. Isobutane, n-butane, t-2 butene, and especially isopentane are enriched in evaporated gasoline. MTBE (methyl-*t*-butyl ether) stands out as a large constituent of all gasoline–related emissions that clearly separates these from diesel in areas where it is used as an additive. These differences are sufficient for CMB separation of gasoline exhaust from liquid and evaporated gasoline, and often from diesel exhaust, in ambient air. Gasoline compositions vary with location and time of year. Liquid gasoline and headspace evaporated gasoline samples should be analyzed at times and places consistent with ambient VOC measurements.

Petrochemical production, especially the refining of gasoline and other fuel oils (Sexton and Westberg, 1979, 1983), can be a large contributor in areas such as Houston, TX (Fujita et al., 1995a) as evidenced in Table 1 for samples taken in and around a refinery. Ethane, propene, propane, n-pentane, t-2 hexene, benzene, n-heptane, toluene, and n-octane are abundant species. Most of these overlap with liquid and evaporated gasoline vapors. Of particular note is the large fraction of unidentified NMHC that constitutes 28% of NMHC in the Table 1 example. This fraction includes real, but unreported, chemical compounds that are not in the other profiles. If properly quantified, these could probably assist the CMB resolution of refinery and other petrochemical sources.

Although solvents from paints and industrial uses are large components of all ROG inventories, their reported profiles are few (Kitto et al., 1997; Guo et al., 1998, 1999). Censullo et al. (1996) evaluated a large number of different solvent uses in southern California, and two profiles are listed in Table 1. These profiles are depleted in the species common to fuel use and production, with larger abundances of styrene, n-decane, and especially "other" compounds. The "other" VOCs are quantified and differ substantially among the different coatings tested. These are sufficient to separate various coating and solvent emissions from other contributors. California requires special solvent and coating formulations to comply with air quality emissions requirements, so these profiles are likely to be very specific to a particular area.

Printing ink solvents from offset (Wadden et al., 1995) and rotogravure are commonly identified in emissions inventories. Most of these emissions are captured, condensed, and re-used by modern printing facilities, especially the toluene used for thinning rotogravure inks. The final column of Table 1 shows enrichments for styrene, n-nonane, and 1,2,4-trimethylbenzene, similar to the other solvents. Specifying abundances of compounds in the "other identified" category often allows the separation of different solvent contributions to ambient VOCs.

In addition to these common emissions sources, landfills are sometimes identified as large TOG emitters owing to their prodigious production of methane that may be accompanied by ROG, depending on the nature of the landfill wastes and disposal practices. Brosseau and Heitz (1994) found acetone, alpha terpinene, benzene, butyl alcohol, dichlorobenzene, dichloromethane, ethylbenzene, ethyl mercaptan, limonene, furans, terpenes, toluene, vinyl acetate, vinyl chloride, and xylene to be among the most abundant components of landfill ROG. Several of these compounds, such as vinyl chloride, are not common to widespread area sources and might be used to determine landfill source contributions by CMB. Kalman (1986) identifies several VOCs outgassed by plastics when they are heated. Acetone was consistently the most abundant ROG found in emissions from the surveyed landfills, probably resulting from the anaerobic decay of discarded organic material. Similar reactions in dumpsters and trash cans, as well as in the natural environment, may account for a portion of the unexplained acetone observed by Fujita et al. (1994) in Los Angeles and by Singh et al. (1994) at more remote locations. Acetone is also a product of photochemistry. Shonnard and Bell (1993) document substantial quantities of benzene emanating from contaminated soil, a situation that will presumably improve as modern amelioration methods are applied to these dumpsites (Fox, 1996).

Garcia et al. (1992) found small quantities of VOC emitted by several French coal-fired power stations, with benzene, toluene, ethylbenzene, xylenes, tetrachloroethane, benzaldehyde, and phenol being the most abundant compounds. Abundances of these compounds were substantially enriched over their abundances in the fuel, indicating that these compounds do not combust as well as other fuel components or that they form as part of the combustion process. Some data have also been

Table 1
Examples of VOC source profiles as a fraction of the sum of 55 photochemical assessment monitoring station (PAMS) compounds

PAMS compound	Average abundances from several representative samples ± standard deviation of these abundances							
	Heavy-duty diesel exhaust[a]	Light-duty gasoline exhaust[b]	Liquid gasoline[c]	Evaporated gasoline[d]	Refinery fugitives[e]	Industrial coating[f]	Primers and enamel[g]	Printing[h]
Ethene	0.107 ± 0.018	0.067 ± 0.008	0.000 ± 0.000	0.000 ± 0.001	0.254 ± 0.200	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
Acetylene	0.019 ± 0.007	0.074 ± 0.011	0.000 ± 0.002	0.000 ± 0.001	0.004 ± 0.002	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
Ethane	0.005 ± 0.005	0.015 ± 0.004	0.000 ± 0.000	0.000 ± 0.001	0.003 ± 0.001	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
Propene	0.049 ± 0.010	0.016 ± 0.005	0.000 ± 0.000	0.000 ± 0.000	0.098 ± 0.116	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
n-Propane	0.010 ± 0.006	0.003 ± 0.006	0.001 ± 0.001	0.009 ± 0.003	0.092 ± 0.125	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
Isobutane	0.009 ± 0.004	0.004 ± 0.003	0.008 ± 0.006	0.030 ± 0.010	0.321 ± 0.279	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
1-Butene	0.036 ± 0.008	0.033 ± 0.003	0.001 ± 0.001	0.007 ± 0.002	0.000 ± 0.001	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
n-Butane	0.029 ± 0.017	0.015 ± 0.003	0.044 ± 0.032	0.087 ± 0.027	0.003 ± 0.001	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
t-2-Butene	0.000 ± 0.002	0.005 ± 0.000	0.002 ± 0.001	0.008 ± 0.002	0.000 ± 0.001	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
c-2-Butene	0.004 ± 0.002	0.003 ± 0.000	0.002 ± 0.001	0.007 ± 0.002	0.000 ± 0.001	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
Isopentane	0.093 ± 0.058	0.091 ± 0.014	0.105 ± 0.021	0.239 ± 0.060	0.000 ± 0.000	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
1-Pentene	0.010 ± 0.003	0.003 ± 0.000	0.003 ± 0.002	0.007 ± 0.002	0.000 ± 0.001	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
n-Pentane	0.028 ± 0.023	0.034 ± 0.002	0.035 ± 0.012	0.060 ± 0.013	0.000 ± 0.000	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
Isoprene	0.005 ± 0.002	0.003 ± 0.001	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.001	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
t-2-Pentene	0.008 ± 0.006	0.005 ± 0.001	0.008 ± 0.003	0.014 ± 0.003	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001
c-2-Pentene	0.003 ± 0.003	0.003 ± 0.000	0.004 ± 0.002	0.007 ± 0.001	0.000 ± 0.001	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
2,2-Dimethylbutane	0.037 ± 0.010	0.001 ± 0.000	0.003 ± 0.004	0.005 ± 0.001	0.000 ± 0.001	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
Cyclopentane	0.003 ± 0.004	0.005 ± 0.000	0.003 ± 0.003	0.006 ± 0.001	0.000 ± 0.001	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
2,3-Dimethylbutane	0.010 ± 0.006	0.011 ± 0.003	0.018 ± 0.006	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
2-Methylpentane	0.030 ± 0.023	0.036 ± 0.005	0.048 ± 0.014	0.046 ± 0.007	0.000 ± 0.001	0.000 ± 0.007	0.000 ± 0.000	0.000 ± 0.006
3-Methylpentane	0.019 ± 0.014	0.021 ± 0.001	0.029 ± 0.008	0.026 ± 0.004	0.000 ± 0.001	0.000 ± 0.007	0.000 ± 0.005	0.003 ± 0.001
2-Methyl-1-pentene	0.013 ± 0.004	0.001 ± 0.002	0.002 ± 0.001	0.002 ± 0.000	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001
n-Hexane	0.019 ± 0.011	0.022 ± 0.014	0.024 ± 0.008	0.018 ± 0.004	0.054 ± 0.067	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
Methylcyclopentane	0.011 ± 0.010	0.031 ± 0.024	0.034 ± 0.013	0.029 ± 0.007	0.000 ± 0.001	0.001 ± 0.000	0.000 ± 0.005	0.000 ± 0.006
2,4-Dimethylpentane	0.004 ± 0.003	0.015 ± 0.007	0.020 ± 0.011	0.013 ± 0.006	0.000 ± 0.001	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
Benzene	0.042 ± 0.015	0.042 ± 0.002	0.013 ± 0.004	0.012 ± 0.003	0.088 ± 0.129	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
Cyclohexane	0.004 ± 0.004	0.008 ± 0.001	0.005 ± 0.006	0.007 ± 0.003	0.002 ± 0.001	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
2-Methylhexane	0.000 ± 0.001	0.021 ± 0.009	0.023 ± 0.005	0.016 ± 0.005	0.000 ± 0.001	0.000 ± 0.007	0.001 ± 0.000	0.000 ± 0.006
2,3-Dimethylpentane	0.006 ± 0.003	0.022 ± 0.005	0.035 ± 0.027	0.022 ± 0.015	0.000 ± 0.001	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
3-Methylhexane	0.012 ± 0.006	0.016 ± 0.001	0.025 ± 0.004	0.017 ± 0.005	0.000 ± 0.001	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
2,2,4-Trimethylpentane	0.020 ± 0.011	0.033 ± 0.011	0.050 ± 0.035	0.033 ± 0.019	0.000 ± 0.001	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
n-Heptane	0.009 ± 0.005	0.007 ± 0.003	0.016 ± 0.003	0.011 ± 0.003	0.000 ± 0.001	0.000 ± 0.007	0.006 ± 0.002	0.000 ± 0.006
Methylcyclohexane	0.005 ± 0.004	0.012 ± 0.003	0.010 ± 0.005	0.009 ± 0.004	0.000 ± 0.001	0.006 ± 0.002	0.014 ± 0.003	0.000 ± 0.006
2,3,4-Trimethylpentane	0.006 ± 0.005	0.012 ± 0.002	0.023 ± 0.016	0.014 ± 0.011	0.000 ± 0.001	0.003 ± 0.001	0.000 ± 0.005	0.000 ± 0.006
Toluene	0.068 ± 0.038	0.089 ± 0.005	0.106 ± 0.029	0.077 ± 0.027	0.004 ± 0.002	0.000 ± 0.007	0.086 ± 0.021	0.004 ± 0.001
2-Methylheptane	0.008 ± 0.010	0.007 ± 0.001	0.010 ± 0.002	0.006 ± 0.002	0.000 ± 0.001	0.038 ± 0.010	0.010 ± 0.002	0.000 ± 0.006
3-Methylheptane	0.006 ± 0.004	0.009 ± 0.001	0.010 ± 0.002	0.007 ± 0.002	0.000 ± 0.001	0.032 ± 0.008	0.007 ± 0.002	0.000 ± 0.006
n-Octane	0.007 ± 0.002	0.005 ± 0.001	0.008 ± 0.002	0.005 ± 0.002	0.000 ± 0.001	0.087 ± 0.022	0.028 ± 0.007	0.002 ± 0.001
Ethylbenzene	0.012 ± 0.009	0.014 ± 0.002	0.022 ± 0.005	0.013 ± 0.004	0.001 ± 0.001	0.026 ± 0.006	0.045 ± 0.011	0.043 ± 0.011
Mp-Xylene	0.053 ± 0.035	0.065 ± 0.006	0.092 ± 0.018	0.057 ± 0.018	0.000 ± 0.001	0.093 ± 0.023	0.169 ± 0.042	0.155 ± 0.039
Styrene	0.014 ± 0.003	0.002 ± 0.001	0.000 ± 0.002	0.001 ± 0.001	0.008 ± 0.004	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
o-Xylene	0.021 ± 0.014	0.023 ± 0.003	0.035 ± 0.007	0.020 ± 0.007	0.000 ± 0.000	0.043 ± 0.011	0.092 ± 0.023	0.062 ± 0.015

n-Nonane	0.006 ± 0.001	0.001 ± 0.000	0.003 ± 0.001	0.002 ± 0.001	0.000 ± 0.001	0.000 ± 0.007	0.028 ± 0.007	0.083 ± 0.021
Isopropylbenzene	0.004 ± 0.004	0.002 ± 0.001	0.002 ± 0.001	0.000 ± 0.000	0.068 ± 0.118	0.005 ± 0.001	0.009 ± 0.002	0.007 ± 0.002
n-Propylbenzene	0.005 ± 0.004	0.003 ± 0.000	0.007 ± 0.001	0.003 ± 0.001	0.000 ± 0.001	0.010 ± 0.002	0.013 ± 0.003	0.024 ± 0.006
m-Ethyltoluene	0.020 ± 0.011	0.017 ± 0.002	0.024 ± 0.004	0.011 ± 0.004	0.000 ± 0.001	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
p-Ethyltoluene	0.008 ± 0.005	0.007 ± 0.001	0.011 ± 0.002	0.005 ± 0.002	0.000 ± 0.001	0.042 ± 0.010	0.043 ± 0.011	0.063 ± 0.016
1,3,5-Trimethylbenzene	0.011 ± 0.006	0.010 ± 0.001	0.013 ± 0.002	0.006 ± 0.002	0.000 ± 0.001	0.044 ± 0.011	0.036 ± 0.009	0.078 ± 0.020
o-Ethyltoluene	0.015 ± 0.006	0.005 ± 0.001	0.009 ± 0.002	0.004 ± 0.001	0.000 ± 0.001	0.000 ± 0.007	0.000 ± 0.005	0.000 ± 0.006
1,2,4-Trimethylbenzene	0.033 ± 0.020	0.037 ± 0.017	0.043 ± 0.009	0.019 ± 0.008	0.000 ± 0.001	0.118 ± 0.030	0.160 ± 0.040	0.142 ± 0.036
n-Decane	0.017 ± 0.001	0.001 ± 0.000	0.002 ± 0.001	0.001 ± 0.000	0.000 ± 0.001	0.299 ± 0.075	0.169 ± 0.042	0.207 ± 0.052
1,2,3-Trimethylbenzene	0.011 ± 0.005	0.007 ± 0.001	0.009 ± 0.002	0.004 ± 0.002	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001
m-Diethylbenzene	0.000 ± 0.001	0.003 ± 0.001	0.002 ± 0.001	0.000 ± 0.000	0.000 ± 0.001	0.000 ± 0.007	0.006 ± 0.002	0.008 ± 0.002
p-Diethylbenzene	0.000 ± 0.001	0.006 ± 0.005	0.000 ± 0.002	0.001 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001
n-Undecane	0.031 ± 0.002	0.000 ± 0.001	0.001 ± 0.001	0.000 ± 0.000	0.000 ± 0.001	0.153 ± 0.038	0.079 ± 0.020	0.118 ± 0.030
Other identified hydrocarbons	0.131 ± 0.013	0.145 ± 0.022	0.147 ± 0.029	0.095 ± 0.016	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001
Unidentified hydrocarbons	0.007 ± 0.001	0.057 ± 0.034	0.239 ± 0.059	0.060 ± 0.021	0.206 ± 0.426	2.451 ± 0.613	1.675 ± 0.419	2.198 ± 0.549
Methyl-*t*-butyl ether	0.000 ± 0.001	0.067 ± 0.017	0.154 ± 0.061	0.194 ± 0.021	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001
Total NMHC	1.138 ± 0.114	1.202 ± 0.120	1.385 ± 0.139	1.155 ± 0.115	1.206 ± 0.121	3.451 ± 0.345	2.675 ± 0.267	3.198 ± 0.320

[a]Tuscarora Tunnel heavy-duty emissions.
[b]Van Nuys tunnel emissions (Fujita et al., 1997a).
[c]Los Angeles liquid gasoline composite (Fujita et al., 1997a).
[d]Los Angeles headspace vapor composite (Fujita et al., 1997a).
[e]COAST fugitive emissions from Houston petroleum industries (Fujita et al., 1995a).
[f]Solvent-based industrial maintenance coatings (Censullo et al., 1996).
[g]Coating profile, quick dry primers and enamels (Censullo et al., 1996).
[h]Coating profile, graphic arts coatings (Censullo et al., 1996).

reported for meat cooking (Schauer et al., 1999) petroleum fires (Booher and Janke, 1997), food and beverage production (Passant et al., 1993), household products and indoor building materials (Sack et al., 1992), ferry boats (Cooper et al., 1996), hot asphalt application (Kitto et al., 1997), fish rendering (Ohira et al., 1976), and phytoplankton in the ocean (McKay et al., 1996).

Biogenic VOC emissions from trees and shrubs (Altshuller, 1983; Roberts et al., 1985; Hewitt and Street, 1992; Tanner and Zielinska, 1994; Benjamin et al., 1997; Street et al., 1997) are typically reported for isoprene and monoterpenes such as alpha- and beta-pinene. These compounds are very reactive and are usually detected only in forested areas. Isidorov et al. (1985) found a wide variety of heavy hydrocarbons in air dominated by different types of plants and trees that might be more stable indicators of biogenic contributions to ambient VOCs.

Variations in biogenic emissions source profiles are difficult to quantify due to the variability in vegetation types, ambient temperature, seasonal growth cycles, and degree of drought. Despite its high reactivity, isoprene is commonly used as marker for biogenic emissions. Terpenes are not often quantified in ambient samples owing to measurement difficulties. Although the effects of photochemical reactions on the source contributions can be minimized for other major hydrocarbon sources by using CMB fitting species with lifetimes comparable to air mass residence times, this is not possible for a single–species biogenic profile based upon isoprene with input data from conventional VOC measurement methods.

Biogenic contributions can be distinguished from fossil fuel contributions to ambient VOC by the ^{14}C isotope which is much more abundant in recently living organisms than in ancient coal, oil, and natural gas fuels (Klouda et al., 1996). ^{14}C is conserved with chemical transformations, thereby enabling the participation of biogenic emissions in photochemistry to be quantified by analysis of VOC end products. Vegetative burning (Edgerton et al., 1986; Isidorov et al., 1985; Hurst et al., 1994) has also been identified by its contributions of methyl chloride and retene in ambient air, but the compounds in its NMHC and NMOG emissions are poorly characterized.

The number of published profiles is large for vehicle exhaust and biogenic emissions, but small for other source types. The low number of tests on different ROG emitters indicates a dearth of profile measurements for many sources that may be important precursors for ozone and $PM_{2.5}$.

5. VOC source contributions

Prior to application of the CMB receptor model, source contributions were inferred by comparing ratios of individual VOCs or classes of VOCs observed in the ambient air with corresponding ratios in source samples. Neligan (1962) compared C_2–C_7 hydrocarbons in ambient air from central Los Angeles with the distribution of these groupings in motor vehicle exhaust. Neligan (1962) reported a greater proportion of the lower molecular weight paraffinic hydrocarbons in ambient samples than in exhaust emissions and attributed this discrepancy to contributions from natural gas. Stephens and Burleson (1967) obtained similar results when they examined VOC measurements collected in Riverside, CA, but they discovered that natural gas contributions alone could not explain the propane/ethane ratios in ambient samples. They suggested a combination of gasoline evaporative losses, emissions from oil fields, and natural gas losses to account for ambient concentrations. Kopczynski et al. (1972) estimated that one-third of the hydrocarbon concentration (as C) measured in 1968 at Downtown Los Angeles could be attributed to natural gas and gasoline vapors based on the ratio of total paraffins (less methane) to carbon monoxide (CO) in motor vehicle exhaust and the average CO concentration in the ambient samples.

Several recent CMB and other modeling applications to VOC apportionment are summarized in Table 2. Most of these studies estimated contributions of five to eight source types and used about 25 CMB fitting species in the calculation.

Vehicle exhaust is invariably the major contributor (frequently more than 50%) to NMHC in urban/suburban areas. The gasoline exhaust contribution is typically four times the diesel exhaust contribution. Evaporated gasoline and liquid gasoline are the next most abundant contributors in most areas. Refinery, forest fire, and other industrial source contributions are area specific.

Several of these studies compared proportional source contribution estimates with proportional emissions inventory estimates. For some study locations, these comparisons show that CMB vehicle emission proportions differ substantially from those in the inventory. CMB source contribution estimates for solvents and coatings were sometimes similar to but were also sometimes nearly an order of magnitude lower than those indicated by the inventories. The examples in Table 2 show how CMB can identify potential discrepancies in emissions models that need to be resolved prior to applying chemical transport models.

Continuous VOC monitors have been developed (e.g., Shreffler, 1993; Farmer et al., 1994), and these provide opportunities to apportion sources hourly to compare with hourly emissions estimates (Fujita et al., 1995a). VOC source apportionment should be more common with large data sets being acquired from the PAMS (Evans et al., 1992). These stations are located throughout the US and many acquire hourly VOC measurements (Oliver et al., 1996).

Table 2
Summary of VOC source apportionment studies using CMB and other receptor models

Study, location, and period measurements	Source apportionment method	Findings
San Joaquin Valley and San Francisco Bay Area, CA (7/90–8/90) (Fujita et al., 1995b) 2-h C_2–C_{11} canister and carbonyl DNPH[a] samples at 0800, 1000, 1200, and 1400 PDT at 34 sites in central California representing urban, non-urban, oilfield background, and forested areas. NMOG = mass equivalent sum of all GC peaks from canister sample plus carbonyls from DNPH	Effective variance weighted least-squares CMB with motor vehicle exhaust, gasoline evaporation, liquid gasoline, CNG[b], GNG[c], LPG[d], oil production, architectural coatings, industrial solvents and coatings, biogenics, and acetone profiles from other studies 26 stable species used in CMB calculation with 57 other species in profiles and ambient data for validation	*Average contributions (%) to NMOG* Vehicle exhaust: 35–70 Gasoline evaporation: 10–40 Coatings and solvents: 1–20 Oil production: 30–50 (southern sites near oilfields), 5–15 (other sites) Biogenic: 10–15 (Yosemite and Sequoia only, based on measured isoprene) Others: 2–20 (morning), 20–60 (afternoon) Ambient motor vehicle contributions were ~ twice proportions from inventory in neighboring grid squares
Los Angeles, CA (8/86) (Harley et al., 1992). Hourly, 4-, and 8-h C_2–C_{10} canister samples collected at 0400, 0600, 0800, and 1100 PDT at 9 sites between 8/10/86 and 8/21/86	Effective variance least-squares CMB with revised and respeciated orgainic gas emissions profiles for gasoline engine exhaust (non-catalyst, catalyst), unburned gasoline (whole liquid gasoline, headspace gasoline vapor), commercial jet exhaust, architectural coatings (solvent-borne, water-borne, thinning solvents), industrial coatings, and industrial adhesives	*Average contributions (%) to NMOC* Gasoline engine exhaust: 31–37 Whole liquid gasoline: 32–38 Headspace gasoline vapor: 5–13 Waste and natural gas: 10–15 Dry cleaning: 0–14 Degreasing solvents: 5–12 Respeciation of organic gas emissions resulted in large changes in basin-wide emission estimates for 1,3-butadine, ethylene glycol, methanol, and cyclohexane. Reactivity for surface coatings and thinning solvents are revised Proportional comparisons between CMB and the emissions inventory found higher unburned gasoline contributions in air samples than in the inventory. Excess unburned gasoline is suspected to be a combination of emissions from tailpipe, hot-soak evaporative, and fuel spillage

Table 2. (*continued*)

Study, location, and period measurements	Source apportionment method	Findings
Los Angeles, CA (7/95 to 10/95) (Fujita et al., 1997a) 3-hour C_2–C_{11} canister samples starting at 0700 and 1400 PDT for six 7-day periods at 3 CARB[e] sites and for 3-day periods at 8 Coordinating Research Council (CRC) sites NMHC = Mass equivalent sum of all GC hydrocarbon peaks from canister	Effective variance weighted least-squares CMB with motor vehicle exhaust (including tunnel, garage, roadside, and dynamometer for light-duty gasoline and diesel exhaust), gasoline evaporation, liquid gasoline, gasoline vapor, CNG, GNG, LPG, architectural coatings, industrial solvents and coatings, and biogenic profiles 27 stable species used in CMB calculation with 56 other species in profiles and ambient data for validation	*Average contributions (%) to sum of NMHC and MTBE with 10 alternative gasoline vehicle profiles* 3 CARB[e] sites / 8 CRC sites Diesel vehicle exhaust: 11–15 / 10–15 Light-duty vehicle exhaust: 38–50 / 42–54 Liquid gasoline: 0.6–11 / 1–14 Gasoline vapour: 15–29 / 10–20 Gas (CNG): 3.1–3.7 / 2.2–2.7 Gas (GNG): 5.2–8.7 / 6.6–8.6 Gas (LPG): 2.6–3.7 / 1.9–3.0 Biogenics: 0.2–0.3 / 0.1–0.2 Coatings (architectural): 3.2–5 / 0.3–1.1 Coatings (industrial): 1.7–9.3 / 4.1–6.9 Coatings (other): 1.7–10 / 1.1–8.9 Unexplained: − 11–3.5 / − 0.9–7.8 Ratios of tailpipe to evaporative emissions were 2.4 in the morning and 1.7 in the afternoon. Morning samples attribute 48% of VOC to vehicle exhaust and 20% to evaporative emissions Heavy-duty diesel hydrocarbons were twice those of light-duty gasoline vehicles on a per-mile basis. About 50% of diesel emissions were $> C_{10}$ species Motor-vehicle-related emissions and sources of ethane and propane gas accounted for > 90% of ambient NMHC. Evidence of emissions from solvent use were found, but much lower than the 30–40% identified in the inventory
1996 Phoenix Ozone Study, Phoenix, AZ (summer, 1996) (Fujita and Lu, 1998a) 4-hour C_2–C_{11} canister samples beginning at 0700 and 1130 at two sites and at 0700 at one site NMHC = sum of all GC hydrocarbon peaks from canister	Effective variance weighted least-squares CMB with motor vehicle exhaust (including tunnel, garage, roadside, and dynamometer for light-duty gasoline and diesel exhaust), gasoline evaporation, liquid gasoline, gasoline vapor, CNG, GNG, LPG, architectural coatings, industrial solvents and coatings, and biogenic profiles 27 stable species used in CMB calculation with 56 other species in profiles and ambient data for validation	*Average contributions (%) to NMHC at 3 sites* Diesel exhaust: 5.4–11.7 Gasoline exhaust: 51.5–59.0 Liquid gasoline: 6.6–8.9 Gasoline vapor: 2.8–7.3 Gas (CNG): 1.2–3.2 Gas (GNG): 5.6–8.0 Gas (LPG): 0.5–1.0 Biogenics: 0.2–2.6 Coatings (architectural): 0.4–2.2 Coatings (industrial): 2.2–3.1 Unexplained: 7–8 Because of the reactivity of isoprene, biogenic contributions are lower limits. Actual contributions may be 5–10 times higher than CMB estimates. Emissions inventory comparison were not made

Coastal Oxidant Assessment for Southeast Texas (COAST) Study, Houston, TX (7/93–8/93) (Fujita et al., 1995a) Hourly canister (C_2–C_{10} HC) and DNPH cartridge (C_1–C_7 carbonyl compounds) from 6 surface sites, 6 times per day, during summer 1993. Measurements aloft (aircraft) starting ~0600 and ~1200 CDT each day at 6 locations. Hourly auto-GC[f] measurements at 2 sites NMHC = sum of all GC hydrocarbon peaks from canister	Effective variance weighted least-squares CMB with motor vehicle exhaust, gasoline evaporation, liquid gasoline, gasoline vapor, CNG, GNG, LPG, architectural coatings, industrial solvents and coatings, and biogenic profiles from CARB's[e] modeling emissions data system and auto/oil program 27 stable species used in CMB calculation with 34 other species in profiles and ambient data for validation	*Average contributions (%) to NMHC* 2 auto-GC sites / 6 surface sites / 6 aloft Vehicle exhaust: 19–27 / 19–36 / 17–39 Liquid gasoline: 12–15 / 7–15 / 1–12 Gasoline vapor: 13–14 / 7–20 / 0–11 CNG: 11–12 / 3.5–6.4 / 8–16 Industrial: 9–18 / 22–50 / 19–52 Biogenic: 0.4–1.6 / 0.5–1.8 / 0.1–7 Unexplained: 22–27 / −2–16 / −1–39 Vehicle exhaust and industrial sources (e.g., refinery) were the largest NMHC contributors. Source contributions aloft were 20% of those found at the surface. The emissions inventory showed higher biogenic emissions, but was comparable for the sum of liquid gasoline, gasoline vapor, industrial, and gas (CNG)
Chicago, IL (7/87–9/87) (Scheff and Wadden, 1993) 4-h C_2–C_7 and Tenax trap (aromatic and chlorinated) samples from 0800 and 1200 CDT at 3 downtown Chicago sites. 20-h samples starting at 1200 CDT at one central city site NMOC = sum of 23 organic compounds (including C_2–C_7, alkanes, and aromatic and chlorinated compounds) analyzed by GC/FID and GC/MS	Ordinary least-squares CMB with 8 profiles (vehicle exhaust, gasoline vapor, architectural coatings, graphic arts, vapor degreasing, dry cleaning, wastewater treatment, and petroleum refining) 23 stable species used in CMB calculation	*Average contributions (%) to NMOC* CMB calculated / Emissions inventory Vehicle exhaust: 21 / 39 Gasoline vapor: 7.1 / 7.6 Solvent (architectural coating): 3.1 / 5.5 Solvent (graphic arts): 1.0 / 9.8 Vapor degreasing: 3.4 / 3.1 Dry cleaning: 0.3 / 0.1 Industry (refining): 7.4 / 1.3 Largest discrepancies were found for petroleum refining contributions between the CMB-calculated and emissions inventory estimates
Detroit, MI (7/88–8/88) (Chung et al., 1996) 1-h canister samples at 0600, 0800, 1200, 1400, and 2200 CDT at 18 sites NMHC = sum of 24 abundant hydrocarbons	Ordinary weighted least-squares CMB with vehicle exhaust, gasoline vapor, petrochemical, architectural coatings, graphic arts, polyethylene, refinery, and coke oven profiles from other studies Sensitivity tests with 18 stable and 24 reactive species yielded similar source contribution estimates	*Average contributions (%) to NMHC* CMB calculated / Emissions inventory Vehicle exhaust: 28 / 33 Gasoline vapor: 9 / 7 Solvent (architectural coating): 2.5 / 3.8 Solvent (graphic arts): 4.7 / 0.7 Industry (refinery): 17 / 0.7

Table 2. (*continued*)

Study, location, and period measurements	Source apportionment method	Findings		
		Industry (coke oven)	3.7	2.0
		Other	35	39
		CMB source contributions were used to verify the emissions inventory estimates prior to ozone modeling		
Southeast Michigan Ozone Study (SEMOS), Detroit, MI (7/93–8/93) (Scheff et al., 1996) 2-h canister C_2–C_{10} samples at 0600, 1000, and 1400 CDT at 4 sites for 8 days during summer 1993 NMOC = sum of chromatographic peaks	Ordinary weighted least-squares CMB with vehicle exhaust, gasoline vapor, petrochemical, architectural coatings, graphic arts, polyethylene, refinery, and coke oven profiles from other studies Sensitivity tests with 18 stable and 24 reactive species yielded similar source contribution estimates	*Average contributions (%) to NMOC*		
		Vehicle exhaust	37–40	
		Liquid gasoline	2–9	
		Gasoline vapor	1–3	
		Solvent (architectural coating)	2–5	
		Solvent (graphic arts)	1–4	
		Industry (refinery)	3–10	
		Industry (coke ovens)	1–4	
		Percent of total NMOC explained by CMB ranged from 54% during afternoon to 69% during early evening (i.e., 1800 CDT). Good agreement between CMB and emissions inventory for sum of vehicle and gasoline, architectural coatings, and coke ovens. CMB found higher proportional contributions from refinery and graphic arts compared to the inventory		
Beaumont, TX, Detroit, MI, Chicago, IL, Washington, DC, and Atlanta, GA (summers of 1984–1988) (Kenski et al., 1995) 1-h and 3-h C_2–C_{10} canister samples at 0600 and 0900 CDT, except at Detroit with 1-h samples at 0600, 0900, 1200, 1400, and 2200 CDT NMHC = sum of 24 abundant hydrocarbons	Ordinary weighted least-squares CMB with vehicle exhaust, gasoline vapor, petrochemical, architectural coatings, graphic arts, polyethylene, refinery, and coke oven profiles from other studies Sensitivity tests with 18 stable and 24 reactive species yielded similar source contribution estimates	*Average contributions (%) to NMHC*		
		Vehicle exhaust	28–55	
		Gasoline vapor	9–20	
		Solvent (architectural coating)	2–6	
		Solvent (graphic arts)	5–12	
		Industry (refinery)	9–17 (in cities with refineries)	
		Industry (coke ovens)	4 (in Detroit and Washington only)	
		Polyethylene	7 (in Beaumont only)	
		Proportional motor vehicle fractions agreed with inventories, but refinery and graphic arts proportions were substantially different		

1995 NARSTO[g]-Northeast Ozone Study (6/95–8/95) (Fujita and Lu, 1998b) Four, 3-h C_2–C_{11} canister samples at five sites and three, 3-h samples at three sites. Also 13, hourly auto-GC and 7 canister-based PAMS sites operated by state and local air pollution agencies in the northeastern states NMHC = sum of all GC hydrocarbon peaks from canister	Effective variance weighted least-squares CMB with motor vehicle exhaust (including tunnel, garage, roadside, and dynamometer for light-duty gasoline and diesel exhaust), gasoline evaporation, liquid gasoline, gasoline vapor, CNG, LPG, and biogenic profiles 27 stable species used in CMB calculation with 56 other species in profiles and ambient data for validation	*Average contribution (%) to NMHC* 10 surface PAMS sites / 6 surface sites / 7 aloft Sites Diesel exhausst: 3–44 / 6–8 / 6–9 Gasoline exhaust: 17–62 / 7–23 / 9–25 Liquid gasoline: 2–9 / 1–7 / 1.5–5.7 Gasoline vapor: 12–31 / 2–6 / 0.8–5.9 CNG: 7–12 / 3–34 / 7–11 LPG: 1–30 / 0.6–3.2 / 0.7–2.4 Biogenic: 1–12 / 2–10 / 0–5.8 Unidentified: / 46–72 / 59–75 Unexplained: − 8–17 / − 4– − 8 / − 6– − 11 Unidentified compounds were the largest fraction of total NMHC. NARSTO samples were collected in areas that represent regional air quality, while PAMS sites represent urban/suburban areas
1990 Atlanta Ozone Precursor Study, Atlanta, GA (7/9–8/90) (Lin and Milford, 1994; Lewis et al., 1993) Hourly C_2–C_{10} canister samples with auto-GC at 2 sites NMOC = 54 hydrocarbon species with ethane excluded	Source profiles were decay-adjusted to account for different reaction rates of VOCs for roadway vehicle and gasoline vapor emissions. PCA[h], CMB, and decay-adjusted CMB were applied to test synthetic and ambient data. 13 stable species used in CMB calculation with 36 other species in profiles and ambient data for validation	Decay factors assumed for propylene were 0.78–0.92 (morning samples), 0.41–0.60 (afternoon samples), and 0.59 to 0.76 (average) *Adjusted CMB source contributions (%) to NMHC* CMB calculated / Lewis et al. (1993) Roadway vehicle emissions: 61–65 / 44 Whole gasoline: Not calculated / 15 Headspace gasoline vapor: 4–8.2 / 4 Total vehicle-related sources in summer 1990: 66–73 / 62 Similar results from Lin and Milford (1994) and Lewis et al. (1993) for separate apportionments when whole gasoline and vehicle exhaust contributions are combined. CMB adjusted for decay factor gives small improvements to CMB fit

[a] DNPH = C_{18} cartridge impregnated with 2,4-dinitrophenylhydrazine.
[b] CNG = compressed natural gas.
[c] GNG = geogenic natural gas.
[d] LPG = liquefied petroleum gas.
[e] California Air Resources Board, Sacramento, CA.
[f] Auto-GC = automated gas chromatography with flame ionization detector (FID).
[g] North American Research Strategy for Tropospheric Ozone.
[h] PCA = principal component analysis.

6. CMB, emissions inventories, and air quality models

CMB plays three roles in air quality assessment. The first is the direct apportionment of ambient concentrations to their sources. This apportionment in and of itself has been of great utility in developing control strategies in PM_{10} non-attainment areas over the past decade. CMB has been the primary analysis tool in areas with intermittent and poorly quantified emissions rates for fugitive dust and wood smoke, and with the highest concentrations occurring under stagnant conditions where air quality dispersion models are inapplicable. As shown in Table 2, this direct apportionment has value for formulating primary ROG reduction strategies for ozone precursors, secondary organic aerosol precursors, hazardous air pollutants, and long-lived gases that affect climate.

Second, CMB independently verifies emissions inventories, against which emissions reduction credits are taken, so that expenditures on their improvement may be better focused. Impediments to CMB/inventory reconciliation include non-standardized and incompatible definitions of ROG, chemical compounds, reporting units, and source categories. Methods to deal with these inconsistencies are complicated, but they are feasible and practical to specify and apply.

Finally, CMB offers a framework for evaluating the outputs of complicated air quality models. The most often used criteria of an air quality model is how well its results compare with measured ozone or particle mass concentrations. Good comparisons are often fortuitous, resulting from adjustment of hundreds of different inputs, parameters, and mathematical relationships within acceptable uncertainty bounds to optimize agreement between modeled and observed concentrations for a single variable. Current models calculate concentrations for dozens of primary, intermediate, and end-product species, many of them VOCs. In principle, these models can produce a pattern of concentrations and uncertainties similar to CMB source profiles that could be used by the CMB for a multivariate fit to the ambient data. This is a more complex, and potentially more accurate "profile aging" process, as represented in a simpler context by Lin and Milford (1994) and Harley et al. (1997). The same performance measures of percent mass, *r*-square, chi-square, and difference between calculated and measured concentrations to evaluate a CMB source apportionment (Watson et al., 1998) could, and should, be used to evaluate model outputs and to diagnose modeling deficiencies.

7. Conclusions

The CMB receptor model has apportioned different fractions of VOCs in several urban areas, mostly in the United States. These applications differ in terms of the total fraction apportioned, the calculation method, the chemical compounds used in the calculation, the apportionment units, and the source profiles applied. Nevertheless, they show similar results with respect to the VOC fractions derived from different sources. Gasoline vehicle exhaust, liquid gasoline, and gasoline evaporation contribute up to 50% or more of the ambient VOCs in many of these studies. Relative motor vehicle source contributions determined by CMB range from equivalent to up to twice their proportions in emissions inventories. Coatings and solvent contributions from CMB are much lower than their proportions in emissions inventories. Several measurement and reporting conventions would facilitate CMB analyses of VOC data sets. These include (1) normalizing measured species in source profiles to the sum of 55 commonly measured PAMS hydrocarbons in units of ppbC or $\mu g\,m^{-3}$; (2) reporting results in electronic data files with common mnemonics in ppbC or $\mu g\,m^{-3}$ units; and (3) identifying and reporting currently unidentified peaks in chromatographic spectra.

The CMB is widely applicable to automated GC and canister samples taken in PAMS networks. It can be more effective with additional specialized measurements that include heavy hydrocarbons by Tenax/GC-FID, halocarbons by Canister/GC-ECD, aldehydes by DNPH/HPLC, and a variety of organic compounds in the gas and solid phase by PUF-XAD/GC-MS.

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References

Altshuller, A.P., 1983. Natural volatile organic substances and their effect on air quality in the United States. Atmospheric Environment 17, 2131–2166.

Altshuller, A.P., 1993. Production of aldehydes as primary emissions and from secondary atmospheric reactions of alkenes and alkanes during the night and early morning hours. Atmospheric Environment 27A, 21–32.

Atkinson, R., 1990. Gas-phase tropospheric chemistry of organic compounds: a review. Atmospheric Environment 24A, 1–41.

Bastable, H.G., Rogers, D.P., Schorran, D.E., 1990. Tracers of opportunity and pollutant transport in Southern California. Atmospheric Environment 24, 137–151.

Benjamin, M.T., Sudol, M., Vorsatz, D., Winer, A.M., 1997. A spatially and temporally resolved biogenic hydrocarbon emissions inventory for the California South Coast Air Basin. Atmospheric Environment 31, 3087–3100.

Black, F.M., High, L.E., Lang, J.M., 1980. Composition of automobile evaporative and tailpipe hydrocarbon emissions. Journal of the Air Pollution Control Association 1216–1221.

Booher, L.E., Janke, B., 1997. Air emissions from petroleum hydrocarbon fires during controlled burning. American Industrial Hygiene Association Journal 58, 359–365.

Bowman, F.A., Pilinis, C., Seinfeld, J.H., 1995. Ozone and aerosol productivity of reactive organics. Atmospheric Environment 29, 579–589.

Brosseau, J., Heitz, M., 1994. Trace gas compound emissions from municipal landfill sanitary sites. Atmospheric Environment 28, 285–294.

Calvert, J.G., 1976. Test of the Theory of Ozone Generation in Los Angeles Atmosphere. Environmental Science and Technology 10, 248–256.

Carter, W.P.L., Lurmann, F.W., 1991. Evaluation of a detailed gas-phase atmospheric reaction mechanism using environmental chamber data. Atmospheric Environment 25A, 2771–2806.

Censullo, A.C., Jones, D.R., Wills, M.T., 1996. Improvement of speciation profiles for architectural and industrial maintenance coating operations. Final Report. Prepared for California Air Resources Board, Sacramento, CA, California Polytechnic State University, San Luis Obispo, CA.

Chang, T.Y., Weinstock, B., 1975. Generalized rollback modeling for urban air pollution control. Journal of the Air Pollution Control Association 25, 1033–1037.

Chuang, J.C., Hannan, S.V., Wilson, N.K., 1987. Field comparison of polyurethane foam and XAD-2 resin for air sampling for polynuclear aromatic hydrocarbons. Environmental Science and Technology 21, 798–804.

Chung, J., Wadden, R.A., Scheff, P.A., 1996. Development of ozone-precursor relationships using VOC receptor modeling. Atmospheric Environment 30, 3167–3179.

Clausen, P.A., Wolkoff, P., 1997. Degradation products of Tenax TA formed during sampling and thermal desorption analysis: indicators of reactive species indoors. Atmospheric Environment 31, 715–726.

Cooper, D.A., Peterson, K.R., Simpson, D.W., 1996. Hydrocarbon, PAH and PCB emissions from ferries: a case study in the Skagerak-Kattegatt-Öresund region. Atmospheric Environment 30, 2463–2474.

Currie, L.A., Gerlach, R.W., Lewis, C.W., Balfour, W.D., Cooper, J.A., Dattner, S.L., deCesar, R.T., Gordon, G.E., Heisler, S.L., Hopke, P.K., Shah, J.J., Thurston, G.D., Williamson, H.J., 1984. Interlaboratory comparison of source apportionment procedures: results for simulated data sets. Atmospheric Environment 18, 1517–1537.

deCesar, R.T., Cooper, J.A., 1982. Evaluation of multivariate and chemical mass balance approaches to aerosol source apportionments using synthetic data and an expanded PACS data set. In: Hopke, P.K., Dattner, S.L. (Eds.), Receptor Models Applied to Contemporary Pollution Problems. Air Pollution Control Association, Pittsburgh, PA, pp. 127–140.

Doskey, P.V., Porter, J.A., Scheff, P.A., 1992. Source fingerprints for volatile non-methane hydrocarbons. Journal of Air and Waste Management Association 42, 1437–1445.

Dzubay, T.G., Stevens, R.K., Balfour, W.D., Williamson, H.J., Cooper, J.A., Core, J.E., deCesar, R.T., Crutcher, E.R., Dattner, S.L., Davis, B.L., Heisler, S.L., Shah, J.J., Hopke, P.K., Johnson, D.L., 1984. Interlaboratory comparison of receptor model results for Houston aerosol. Atmospheric Environment 18, 1555–1566.

Edgerton, S.A., Czuczwa, J.M., 1989. Source apportionment of dioxins and dibenzofurans in ambient air in Ohio. In: Watson, J.G. (Ed.), Transactions, Receptor Models in Air Resources Management. Air and Waste Management Association, Pittsburgh, PA, pp. 59–70.

Edgerton, S.A., Khalil, M.A.K., Rasmussen, R.A., 1986. Source emission characterization of residential woodburning stoves and fireplaces: fine particle/methyl chloride ratios for use in chemical mass balance modeling. Environmental Science and Technology 20, 803–807.

Evans, G.F., Lumpkin, T.A., Smith, D.L., Somerville, M.C., 1992. Measurements of VOCs from the PAMS network. Journal of Air and Waste Management Association 42, 1319–1323.

Farmer, C.T., Milne, P.J., Riemer, D.D., Zika, R.G., 1994. Continuous hourly analysis of C_2–C_{10} non-methane hydrocarbon compounds in urban air by GC-FID. Environmental Science and Technology 28, 238–245.

Fox, R.D., 1996. Critical review: physical/chemical treatment of organically contaminated soils and sediments. Journal of Air and Waste Management Association 46, 391–413.

Friedlander, S.K., 1973. Chemical element balances and identification of air pollution sources. Environmental Science and Technology 7, 235–240.

Fujita, E.M., Lu, Z., 1998a. Hydrocarbon receptor modeling for the 1996 Phoenix Ozone Study. Prepared for ENSR Corporation, Camarillo, CA, Desert Research Institute, Reno, NV.

Fujita, E.M., Lu, Z., 1998b. Analysis of data from the 1995 NARSTO-Northeast Study. Volume III: chemical mass balance receptor modeling. Prepared for Coordinating Research Council, Atlanta, GA, Desert Research Institute, Reno, NV.

Fujita, E.M., Watson, J.G., Chow, J.C., Lu, Z., 1994. Validation of the chemical mass balance receptor model applied to hydrocarbon source apportionment in the Southern California Air Quality Study. Environmental Science and Technology 28, 1633–1649.

Fujita, E.M., Lu, Z., Sagebiel, J., Robinson, N.F., Watson, J.G., 1995a. VOC source apportionment for the Coast Oxidant Assessment for Southeast Texas. Prepared for Texas Natural Resource Conservation Commission, Austin, TX, Desert Research Institute, Reno, NV.

Fujita, E.M., Watson, J.G., Chow, J.C., Magliano, K.L., 1995b. Receptor model and emissions inventory source apportionments of nonmethane organic gases in California's San Joaquin Valley and San Francisco Bay Area. Atmospheric Environment 29, 3019–3035.

Fujita, E.M., Lu, Z., Sheetz, L., Harshfield, G., Zielinska, B., 1997a. Determination of mobile source emission source fraction using ambient field measurements. Prepared for Coordinating Research Council, Atlanta, GA, Desert Research Institute, Reno, NV.

Fujita, E.M., Lu, Z., Sheetz, L., Harshfield, G., Hayes, T., Zielinska, B., 1997b. Hydrocarbon source apportionment in western Washington. Prepared for State of Washington Dept. of Ecology, Lacy, WA, Desert Research Institute, Reno, NV.

Garcia, J.P., Beyne-Masclet, S., Mouvier, G., 1992. Emissions of volatile organic compounds by coal-fired power stations. Atmospheric Environment 26A, 1589–1597.

Gertler, A.W., Fujita, E.M., Pierson, W.R., Wittorff, D.N., 1996. Apportionment of NMHC tailpipe vs non-tai;pipe emissions in the Fort McHenry and Tuscarora Mountain tunnels. Atmospheric Environment 30, 2297–2305.

Grosjean, D., 1992. In-situ organic aerosol formation during a smog episode: estimated production and chemical functionality. Atmospheric Environment 26A, 953–963.

Guo, Z., Sparks, L.E., Tichenor, B.A., Chang, J.C.S., 1998. Predicting the emissions of individual VOCs from petroleum-based indoor coatings. Atmospheric Environment 32, 231–238.

Guo, Z., Chang, J.C.S., Sparks, L.E., Fortmann, R.C., 1999. Estimation of the rate of VOC emissions from solvent-based indoor coating materials based on product formulation. Atmospheric Environment 33, 1205–1216.

Harley, R.A., Cass, G.R., 1994. Modeling the concentrations of gas-phase toxic organic air pollutants: direct emissions and atmospheric formation. Environmental Science and Technology 28, 88–98.

Harley, R.A., Hannigan, M.P., Cass, G.R., 1992. Respeciation of organic gas emissions and the detection of excess unburned gasoline in the atmosphere. Environmental Science and Technology 26, 2395–2408.

Harley, R.A., Sawyer, R.F., Milford, J.B., 1997. Updated photochemical modeling for California's South Coast Air Basin: comparison of chemical mechanisms and motor vehicle emission inventories. Environmental Science and Technology 31, 2829–2839.

Haszpra, L., Szilagyi, I., 1994. Non-methane hydrocarbon composition of car exhaust in Hungary. Atmospheric Environment 28, 2609–2614.

Henry, R.C., 1992. Dealing with near collinearity in chemical mass balance receptor models. Atmospheric Environment 26A, 933–938.

Hewitt, C.N., Street, R.A., 1992. A qualitative assessment of the emission of non-methane hydrocarbon compounds from the biosphere to the atmosphere in the U.K.: present knowledge and uncertainties. Atmospheric Environment 26A, 3069–3078.

Hurst, D.F., Griffith, D.W.T., Cook, G.D., 1994. Trace gas emissions from biomass burning in tropical Australian savannas. American Industrial Hygiene Association Journal 99, 16441–16456.

Isidorov, V.A., Zenkevich, I.G., Ioffe, I.G., 1985. Volatile organic compounds in the atmosphere of forests. Atmospheric Environment 19, 1–8.

Javitz, H.S., Watson, J.G., Robinson, N.F., 1988. Performance of the chemical mass balance model with simulated local-scale aerosols. Atmospheric Environment 22, 2309–2322.

Kalman, D., 1986. Survey analysis of volatile organics released from plastics under thermal stress. American Industrial Hygiene Association Journal 47, 270–275.

Kenski, D.M., Wadden, R.A., Scheff, P.A., Lonneman, W.A., 1995. Receptor modeling approach to VOC emission inventory validation. Journal of Environmental Engineering 121, 483–491.

Kim, B.M., Henry, R.C., 1989. Analysis of multicollinearity indicators and influential species for chemical mass balance receptor model. In: Watson, J.G. (Ed.), Transactions, Receptor Models in Air Resources Management. Air & Waste Management Association, Pittsburgh, PA, pp. 379–390.

Kitto, A.M., Pirbazari, M., Badriyha, B.N., Ravindran, V., Tyner, R., Synolakis, C.E., 1997. Emissions of volatile and semi-volatile organic compounds and particulate matter from hot asphalts. Environmental Technology 18, 121–138.

Kleindienst, T.E., Corse, E.W., Blanchard, F.T., Lonneman, W.A., 1998. Evaluation of the performance od DNPH-coated silica gel and C_{18} cartridges in the measurement of formaldehyde in the presence and absence of ozone. Environmental Science and Technology 124–130.

Klouda, G.A., Lewis, C.W., Rasmussen, R.A., Rhoderick, G.C., Sams, R.L., Stevens, R.K., Currie, L.A., Donahue, D.J., Jull, A.J.T., Seila, R.L., 1996. Radiocarbon measurements of atmospheric volatile organic compounds: quantifying the biogenic contribution. Environmental Science and Technology 30, 1098.

Kopczynski, S.L., Lonneman, W.A., Sutterfield, F.D., Darley, P.E., 1972. Photochemistry of atmospheric samples in Los Angeles. Environmental Science and Technology 6, 342–347.

Lewis, C.W., Zweidinger, R.B., 1992. Apportionment of residential indoor aerosol VOC and aldehyde species to indoor and outdoor sources, and their source strengths. Atmospheric Environment 26A, 2179–2184.

Lewis, C.W., Conner, T.L., Stevens, R.K., Collins, J.F., and Henry, R.C., 1993. Receptor modeling of volatile hydrocarbons measured in the 1990 Atlanta Ozone Precursor Study. Paper No. 93-TP-58.04 presented at the 86th Annual Meeting, Denver, CO. Air and Waste Management Association, Pittsburgh, PA.

Lewis, C.W., Shreffler, J.H., Henry, R.C., 1998. An exploratory look at hydrocarbon data from the photochemical assessment monitoring stations network. Journal of Air and Waste Management Association 48, 71–76.

Lin, C., Milford, J.B., 1994. Decay-adjusted chemical mass balance receptor modeling for volatile organic compounds. Atmospheric Environment 28, 3261–3276.

Lowenthal, D.H., Chow, J.C., Watson, J.G., Neuroth, G.R., Robbins, R.B., Shafritz, B.P., Countess, R.J., 1992. The effects of collinearity on the ability to determine aerosol contributions from diesel- and gasoline-powered vehicles using the chemical mass balance model. Atmospheric Environment 26A, 2341–2351.

McKay, W.A., Turner, M.F., Jones, B.M.R., Halliwell, C.M., 1996. Emissions of hydrocarbons from marine phytoplankton – some results from controlled laboratory experiments. Atmospheric Environment 30, 2583–2594.

Meng, Z., Dabdub, D., Seinfeld, J.H., 1997. Chemical coupling between atmospheric ozone and particulate matter. Science 277, 116–118.

Mugica, V., Vega, E., Arriaga, J.L., Ruiz, M.E., 1998. Determination of motor vehicle profiles for non-methane organic compounds in the Mexico City metropolitan area. Journal of Air and Waste Management Association 48, 1060–1068.

Neligan, R.E., 1962. Hydrocarbons in the Los Angeles atmosphere. Archives of Environmental Health 5, 67–77.

Odum, J.R., Jungkamp, T.P.W., Griffin, R.J., Forstner, H.J.L., Flagan, R.C., Seinfeld, J.H., 1997. Aromatics, reformulated gasoline, and atmospheric organic aerosol formation. Environmental Science and Technology 31, 1890–1897.

Ohira, T., Ishuguro, M.T., Koyama, O., 1976. Gas chromatographic analysis of offensive odors at plants handling fish entrails and bones. Japan Society for Air Pollution 2, 58–59.

Oliver, K.D., Adams, J.R., Daughtrey Jr., E.H., McClenny, W.A., Yoong, M.J., Pardee, M.A., 1996. Technique for monitoring ozone precursor hydrocarbons in air at photochemical assessment monitoring stations: sorbent preconcentration, closed-cycle cooler cryofocusing, and GC-FID analysis. Atmospheric Environment 30, 2751–2758.

Pandis, S.N., Harley, R.A., Cass, G.R., Seinfeld, J.H., 1992. Secondary organic aerosol formation and transport. Atmospheric Environment 26A, 2269–2282.

Passant, N.R., Richardson, S.J., Swannell, R.P.J., Gibson, N., Woodfield, M.J., van der Lugt, J.P., Wolsink, J.H., Hesselink, P.G.M., 1993. Emissions of volatile organic compounds (VOCs) from the food and drink industries of the European community. Atmospheric Environment 27A, 2555–2566.

Pellizzari, E.D., Demian, B., Krost, K.J., 1984. Sampling of organic compounds in the presence of reactive inorganic gases with Tenax GC. Analytical Chemistry 56, 793–798.

Pierson, W.R., Gertler, A.W., Robinson, N.F., Sagebiel, J.C., Zielinska, B., Bishop, G.A., Stedman, D.H., Zweidinger, R.B., Ray, W.D., 1996. Real-world automotive emissions – summary of studies in the Fort McHenry and Tuscarora Mountain tunnels. Atmospheric Environment 30, 2233–2256.

Roberts, J.M., Hahn, C.J., Fehsenfeld, F.C., Warnock, J.M., Albritton, D.L., Sievers, R.E., 1985. Monoterpene hydrocarbons in the nighttime troposphere. Environmental Science and Technology 19, 364–369.

Sack, T.M., Steele, D.H., Hammerstrom, K., Remmers, J., 1992. A survey of household products for volatile organic compounds. Atmospheric Environment 26A, 1063–1070.

Sagebiel, J.C., Zielinska, B., Pierson, W.R., Gertler, A.W., 1996. Real-world emissions and calculated reactivities of organic species from motor vehicles. Atmospheric Environment 30, 2287–2296.

Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 1999. Measurement of emissions from air pollution sources. C_1–C_{29} organic compounds from meat charbroiling. Environmental Science and Technology 33, 1566–1577.

Scheff, P.A., Wadden, R.A., 1993. Receptor modeling of volatile organic compounds: 1. Emission inventory and validation. Environmental Science and Technology 27, 617–625.

Scheff, P.A., Wadden, R.A., Bates, B.A., Aronian, P.F., 1989. Source fingerprints for receptor modeling of volatile organics. Journal of the Air Pollution Control Association 39, 469–478.

Scheff, P.A., Wadden, R.A., Kenski, D.M., Chung, J., Wolff, G., 1996. Receptor model evaluation of the Southeast Michigan Ozone Study ambient NMOC measurements. Journal of Air and Waste Management Association 46, 1048–1057.

Seinfeld, J.H., Pandis, S.N., 1997. Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. Wiley, New York, NY.

Sexton, K., Westberg, H.H., 1979. Ambient air measurements of petroleum refinery emissions. Journal of the Air Pollution Control Association 29, 1149–1152.

Sexton, K., Westberg, H.H., 1983. Photochemical ozone formation from petroleum refinery emissions. Atmospheric Environment 17, 467–475.

Shareef, G.S., Butler, W.A., Bravo, L.A., Stockton, M.B., 1988. Air emissions species manual: volatile organic compound species profiles. Report No. EPA-450/2-88-003a. U.S. Environmental Protection Agency, Research Triangle Park, NC.

Shonnard, D.R., Bell, R.L., 1993. Benzene emissions from a contaminated air-dry soil with fluctuations of soil temperature or relative humidity. Environmental Science and Technology 27, 2909–2913.

Shreffler, J.H., 1993. Comparison of nonmethane organic compound concentration data collected by two methods in Atlanta. Journal of Air and Waste Management Association 43, 1576–1584.

Siegl, W.O., Hammerle, R.H., Herrmann, H.M., Wenclawiak, B.W., Luers-Jongen, B., 1999. Organic emissions profile for a light-duty diesel vehicle. Atmospheric Environment 33, 797–806.

Singh, H.B., O'Hara, D., Herlth, D., Sachse, W., Blake, D.R., Bradshaw, J.D., Kanakidou, M., Crutzen, P.J., 1994. Acetone in the atmosphere: distribution, sources, and sinks. Journal of Geophysical Research 99, 1805–1820.

Stephens, E.R., Burleson, F.P., 1967. Analysis of the atmosphere for light hydrocarbons. Journal of the Air Pollution Control Association 17, 147–153.

Street, R.A., Owen, S., Duckham, S.C., Boissard, C., Hewitt, C.N., 1997. Effect of habitat and age on variations in volatile organic compound (VOC) emissions from *Quercus ilex* and *Pinus pinea*. Atmospheric Environment 31, 89–100.

Tanner, R.L., Zielinska, B., 1994. Determination of the biogenic emission rates of species contributing to VOC in the San Joaquin Valley of California. Atmospheric Environment 28, 1113–1120.

U.S. EPA, 1987. Receptor model technical series, Volume III (Revised). CMB user's manual (Version 6.0). Report No. EPA-450/4-83-014R. U.S. Environmental Protection Agency, Research Triangle Park, NC.

U.S. EPA, 1997a. National ambient air quality standards for particulate matter – final rule. Federal Register 62, 38651–38760.

U.S. EPA, 1997b. Compendium method TO-14A: determination of volatile organic compounds (VOCs) in ambient air using specially prepared canisters with subsequent analysis by gas chromatography. Report No. EPA/625/R-96/010b. U.S. Environmental Protection Agency, Cincinnati, OH.

Wadden, R.A., Scheff, P.A., Franke, J.E., Conroy, L.M., Keil, C.B., 1995. Determination of VOC emission rates and compositions for offset printing. Journal of Air and Waste Management Association 45, 547–555.

Wallington, T.J., Andino, J.M., Potts, A.R., Rudy, S.J., Siegl, W.O., Zhang, Z., Kurylo, M.J., Huie, R.E., 1993. Atmospheric chemistry of automotive fuel additives: diisopropyl ether. Environmental Science and Technology 27, 98–104.

Watson, J.G., 1984. Overview of receptor model principles. Journal of the Air Pollution Control Association 34, 619–623.

Watson, J.G., Cooper, J.A., Huntzicker, J.J., 1984. The effective variance weighting for least squares calculations applied to the mass balance receptor model. Atmospheric Environment 18, 1347–1355.

Watson, J.G., Robinson, N.F., Chow, J.C., Henry, R.C., Kim, B.M., Pace, T.G., Meyer, E.L., Nguyen, Q., 1990. The USEPA/DRI chemical mass balance receptor model, CMB 7.0. Environmental Software 5, 38–49.

Watson, J.G., Chow, J.C., Lu, Z., Fujita, E.M., Lowenthal, D.H., Lawson, D.R., 1994. Chemical mass balance source apportionment of PM_{10} during the Southern California Air Quality Study. Aerosol Science and Technology 21, 1–36.

Watson, J.G., Robinson, N.F., Lewis, C.W., Coulter, C.T., Chow, J.C., Fujita, E.M., Conner, T.L., Pace, T.G., 1998. CMB8 applications and validation protocol for $PM_{2.5}$ and VOCs. Report No. 1808.2D1. Prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC, Desert Research Institute, Reno, NV.

Williams, R.L., Lipari, F., Potter, R.A., 1990. Formaldehyde, methanol and hydrocarbon emissions from methanol-fueled cars. Journal of Air and Waste Management Association 40, 747–756.

Zielinska, B., Fujita, E.M., 1994a. Organic gas sampling. In: Markert, B. (Ed.), Environmental Sampling for Trace Analysis. VCH Publishers, New York, NY, pp. 163–184.

Zielinska, B., Fujita, E.M., 1994b. The composition and concentration of hydrocarbons in the range of C_2 to C_{18} in downtown Los Angeles, CA. Research on Chemical Intermediates 20, 321–334.

Zweidinger, R.B., Sigsby Jr., J.E., Tejada, S.B., Stump, F.D., Dropkin, D.L., Ray, W., Duncan, J.W., 1988. Detailed hydrocarbon and aldehyde mobile source emissions from roadway studies. Environmental Science and Technology 22, 956–962.