

**Considerations in the measurement of ambient air and vehicle exhaust to  
support chemical mass balance (CMB) analysis**

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## Abstract

The particles in gasoline and diesel vehicle exhaust carry distinctive combinations of certain chemical compounds. The prominence of their chemical ‘fingerprints’ in ambient particulate matter is thus a qualitative but direct indication of gasoline and diesel vehicles’ relative importance as sources of emissions. Ambient composition can be inverted mathematically to obtain a quantitative estimate of source contributions, but this requires that the chemical composition of all emissions in the ambient mix be accurately known. While the aggregate emissions of the gasoline-fueled and diesel-fueled fleets are chemically distinct from each other, and from other categories of carbonaceous particle emissions such as vegetative burning and meat cooking, individual emissions can differ significantly between vehicles in the same category. A fleet’s exhaust composition can be determined from tests on individual vehicles only if this variation is represented in sample selection and accounted for statistically. This report provides guidance on meeting these and other requirements for source apportionment in a program of vehicle testing.

## Introduction

Recent studies have used detailed chemical analyses as the basis for estimating the contributions of gasoline and diesel vehicle exhaust to ambient particulate matter (PM). This approach consists of accounting for the observed chemical composition of ambient air as an inferred mix of chemically distinct emissions from different source types. Such chemical reconciliation of source and ambient data, known as Chemical Mass Balance (CMB) analysis, is a well established form of receptor-oriented air quality modeling (Watson et al., 1990).

Early CMB analyses relied mainly on elemental composition (determined by X-ray fluorescence or neutron activation), with some additional data on the major inorganic ions, ‘elemental’ carbon, and ‘organic’ carbon (Miller et al., 1972). These studies had only limited chemical resolution with which to distinguish motor vehicle exhaust from wood smoke and other carbonaceous emissions, particularly after tetraethyl lead was phased out of gasoline supplies (Lowenthal et al., 1992). The new studies introduce large quantities of additional information, on the abundance of individual molecular species in the organic carbon fraction. Some of these organic molecules are possible markers for specific fuel stocks or combustion conditions, with the potential to distinguish among different sources of carbonaceous emissions.

This report considers the mathematical structure and statistical requirements of CMB analysis, and is intended to inform planning for a contemplated program of chassis dynamometer and ambient measurements in Los Angeles. Specific issues have been addressed in a series of technical notes that are incorporated as appendices. The following sections review existing data and tools, assess their adequacy for the contemplated application, and recommend a general strategy for new measurements and analyses.

### Previous studies in Los Angeles and Denver

This section reviews the state of CMB practice as it is represented by two published apportionments, Schauer et al. (1996) and Watson et al. (1998). As outlined in Appendix A, each of these studies included coordinated measurements of both ambient air and representative emissions. There exist many other interesting collections of vehicle exhaust data that could be included in a more comprehensive and leisurely review, but most of these are isolated and incomplete from a CMB perspective. The measurements by Miguel et al. (1998) of polycyclic aromatic hydrocarbon (PAH) species and 'elemental' carbon in a northern California highway tunnel are an example of such data.

Schauer et al. (1996) presented a CMB that capped a program of measurements carried out in the Los Angeles basin over several years by a series of investigators under the direction of Professor Glen Cass at Caltech. The analysis integrated ambient data collected in 1982 with source data collected over the subsequent decade, adjusting where necessary for intervening changes in technology. Watson et al. (1998) constructed a CMB based on an intensive measurement campaign in Denver, the Northern Front Range Air Quality Study (NFRAQS, <http://www.nfraqs.colostate.edu>). Ambient and source measurements for NFRAQS were concurrent, and focused on the winter of 1996-97.

Both the Caltech and NFRAQS studies used the detailed speciation of organic aerosol to distinguish carbonaceous particulate matter emitted by different source categories. Both collected exhaust samples from vehicles by standard EPA test procedures on chassis dynamometers, and used standard EPA-approved software to construct their CMBs (Watson et al., 1990). The two studies employed somewhat differing measurement and analysis strategies, however, each incorporating features worth integrating into future work. The following discussion of their strengths and weaknesses should be understood in this planning context; all of the weaknesses in the Caltech and NFRAQS studies resulted from trade-offs imposed by time and resource constraints.

NFRAQS devoted extensive resources to the characterization of emissions from vehicles and other major sources of carbonaceous aerosol. For the winter 1996-97 study, 72 light duty gasoline vehicles and 12 heavy duty diesel trucks and busses were recruited according to predetermined criteria that included weight class, model year grouping, and, in the case of gasoline vehicles, exhaust opacity. Exhaust samples were distinguished by weight class and fuel type, phase of the Federal Test Procedure (FTP), and total emission rate. The Caltech study recruited 13 gasoline vehicles, all cars, and two heavy duty diesel trucks, both with low mileages. Caltech consolidated all exhaust samples into three aggregates, one for the diesels and one each for gasoline vehicles with and without catalysts.

The NFRAQS design provides crucial information on the variability of exhaust composition, not only across different categories but also within categories (Appendices B,C,D). It is this variability that determines the number of test vehicles needed to represent the

population, along with the random error to be expected in the resulting statistics. The lack of such information for the Caltech study, a consequence of its limited resources, was a major limitation of its design. The majority of our planning analyses accordingly rest on the data from NFRAQS.

The Caltech study devoted more attention to the breadth and sensitivity of its chemical analyses. Emissions of primary particulate carbon in the Los Angeles basin were first inventoried to determine the dominant source categories, and analytical methods were then optimized toward quantifying potential markers for those categories. This approach led, for example, to a focus on steranes and triterpanes as compounds with no significant sources other than lubricating oil in vehicle exhaust. Steranes and triterpanes were measured in NFRAQS, but analytical sensitivity was inadequate for their reliable detection in ambient air.

The Caltech and NFRAQS studies both found “elemental” carbon (EC) to be the main individual constituent of diesel exhaust, but yielded sharply differing estimates for the contributions to ambient EC from other sources. The Caltech group attributed about 95% of their ambient EC to diesels, making EC a near-unique marker for diesel exhaust, while NFRAQS attributed one-third to one-half of its ambient EC to non-diesel sources. Much of this difference likely reflects the differing analytical protocols by which the two studies defined their EC fractions. Both methods are well established, and both define EC as the carbon left on a quartz sample filter after specified cycles of heating and oxidation. Both methods monitor sample light absorption to adjust for the pyrolytic conversion of “organic” to “elemental” carbon. The two methods are known to yield differing EC determinations for certain types of carbonaceous material, however, and differences are evident in the source measurements from Caltech and NFRAQS (Appendix E).

The reduction of emissions data to CMB input profiles involves numerous choices (Appendices B,C), and the two studies followed somewhat different strategies in their analyses. The most obvious difference is that the Caltech study used a single profile to represent the aggregate exhaust from all gasoline-fueled vehicles, while NFRAQS used three different profiles for this component, their relative proportions left for the CMB to determine. The Caltech CMB profile was a numerical composite of two profiles based on physically composited samples, one from all catalyst-equipped cars and one from all pre-catalyst cars, with the two profiles weighted by inventory-based estimates of their categories’ aggregate emissions. Each NFRAQS CMB profile was an unweighted numerical composite of several profiles, each constituent profile based on a sample from an individual vehicle group and mode of operation. After some exploration of the data, the several dozen individual profiles were consolidated into three composites: complete FTP for visibly smoking vehicles, FTP bag 1 (cold-start operation) for non-smoking vehicles, and FTP bag 2 (hot-stabilized operation) for non-smoking vehicles.

Each of the two interpretive strategies has its pros and cons. The Caltech approach, using inventory estimates to consolidate all of the gasoline test data into a single profile, allows for the direct incorporation of the best information available from large-scale surveys of fleet

composition, vehicle operation, and maintenance patterns. The drawback to this approach is that the CMB results then incorporate the assumptions made in the inventory. The NFRAQS approach, employing multiple profiles to represent different vehicle categories and operating modes, offers an independent estimate for such inventory parameters as the proportion of smoking vehicles and the mix of cold start and hot stabilized operation. However, the added information comes at the cost of decreased numerical stability and increased uncertainty in the CMB solution.

### Conclusion: the prospects for CMB analysis in Los Angeles

The sustained program of ambient and source measurements carried out at Caltech was a visionary undertaking that established the promise of organic speciation for resolving types of carbonaceous emissions. The intensive NFRAQS study substantially advanced the case for organic speciation by establishing the feasibility of scaling up a source testing program to address issues of source variation and representative sampling. The CMB analyses from both studies are substantially more informative than those from earlier studies with less chemical resolution. In the final analysis, however, both studies leave some significant questions unresolved:

- S How many types of vehicle exhaust need to be distinguished? The chemical composition of gasoline or diesel exhaust is observed to vary with vehicle and operating mode (Appendix C) – how much of this variability is attributable to shifts in the relative proportions of a few basic components like oil blow-by and unburned fuel?
- S Which chemical species are the best indicators of motor vehicle exhaust? Individual exhaust constituents typically vary by factors of two or more as fractions of total emissions (Appendix B) – is there a linear combination of compounds (e.g. a weighted sum of indicators for raw fuel, oil blow-by, and combustion products) that correlates more tightly with total emissions?
- S What is the uncertainty of CMB source estimates when realistic source-profile errors are taken into account? The standard EPA software for CMB analysis does not account for the non-random errors typically generated by the source variability noted above (Appendix D).
- S How sensitive are the CMB source estimates to the method used to determine EC? The differing methods used in the Caltech and NFRAQS apportionments appear to respond differently to different components of the ambient mix (Appendix E).

The Caltech and NFRAQS studies are best viewed as major milestones in the development of an approach to apportionment whose potential yet to be fully realized. From today's planning perspective, the Caltech data for Los Angeles characterize obsolescent vehicle technologies and ancient atmospheric conditions, and offer insufficient information on the variation of emissions within source categories. The NFRAQS data for Denver are fairly current, and better characterize the diversity of emissions from similar sources. 'NFRAQS-like' data – chassis dynamometer exhaust samples analyzed by the same laboratory – are already available for light-duty vehicles in Los Angeles (Norbeck et al., 1998). However the NFRAQS chemical analyses did not deliver the sensitivity and resolution achieved by the Caltech group, and yielded

a shortage of source-specific marker species. The NFRAQS CMB was forced to lean heavily on total 'organic carbon' as a fitting species, precluding any independent test of its chemical closure.

An integrated program of new measurements to characterize both emissions and ambient air is thus necessary if CMB analysis is to improve present apportionments of ambient PM in Los Angeles. A program incorporating the best features of its predecessors would provide better chemical resolution and sensitivity than achieved in NFRAQS, and a more thorough characterization of the vehicle population than undertaken by Caltech. As CMB analyses based on organic molecules are still evolving, and would next be applied to data that are in some respects unprecedented, their accuracy cannot yet be forecast from theory or experience. At a minimum, however, the recommended program should significantly constrain the range of physically plausible source contributions, adding to the reality checks available for apportionments derived by other means.

Recommendations for ambient air and vehicle exhaust measurements to support resolution of gasoline and diesel components in ambient PM

Our first recommendations address the core difficulty facing the use of chemical composition to identify gasoline and diesel vehicle exhaust in ambient air, which is the chemical variability that is empirically observed in emissions (Appendices B,C,D). Our confidence in our apportionment of an ambient air sample will depend on our confidence that we have sampled emissions representative of the source categories influencing that sample (recommendation 1). Our ability to quantify this confidence will in turn depend on our understanding the variation of emissions within those source categories (recommendation 2).

***1a. Sample light-duty vehicles representatively from categories defined by existing state records.*** Use registration records to recruit 20 registered light-duty gasoline vehicles (LDGVs) with no record of ever having failed inspection, and 20 registered LDGVs with past failures in their records. Use 'hot-line' records to recruit 20 LDGVs of any registration status that have been reported for having visible emissions, recording any intervening repairs. To assure representative coverage of the three primary categories, identify target sample numbers for subcategories defined by model year groupings, vehicle types and, for hot-line recruits, repair status. Create randomized lists of qualifying vehicles in each subcategory, and recruit these vehicles in order until quotas are met.

The procedure sketched in recommendation 1a is designed to yield a stratified sample that includes representatives of all major contributors to light-duty vehicle emissions in Los Angeles. (Note that light-duty diesel vehicles are neglected, as minor contributors.) It is not intended to yield a sample fleet that mimics the population of light-duty vehicles in Los Angeles. Because our primary interest is in total emissions, our sampling strategy is biased toward vehicle categories that are expected to contribute disproportionately to this total. Because the bias is explicit, and is based on vehicle characteristics whose population statistics can be estimated from existing records, it can (and should) be eliminated from the composite profiles generated for

CMB analysis: test data from individual vehicle groupings will simply be weighted to reflect the Los Angeles population.

The categories into which vehicles are eventually grouped for CMB analysis need not coincide with the regulatory strata used to guide their recruitment. Past inspection history might fail to exhibit any association with current exhaust composition, for example, in which case there would be no reason to composite the emissions from ‘never-failed’ and ‘ever-failed’ vehicles into separate (and identical) composition profiles. Alternatively, a strong association between exhaust composition and some unanticipated vehicle characteristic might provide a basis for additional *a posteriori* discrimination between vehicle categories.

***1b. Sample heavy-duty vehicles from groups representing varied conditions of maintenance. Recruit 10 to 15 heavy duty diesel vehicles (HDDVs) from truck rental agencies, and 10 to 15 HDDVs from used truck dealerships. Recruit, through owner contact, 5 HDDVs that have either failed the smoke test or been reported as smokers. In each category, identify target sample numbers for various vehicle weight groupings. Recruit two diesel transit buses, one with two stroke engine technology and one with recent four stroke technology.***

Heavy-duty vehicles are much harder than light-duty vehicles to recruit selectively, due to their greater economic value and lesser interchangeability. A different scheme must guide their recruitment in any case, as the California Air Resources Board has no comprehensive I&M program for trucks and buses. Recommendation 1b attempts within these constraints to parallel the strategy outlined in recommendation 1a. The vehicles from truck rental agencies correspond in this scheme to the LDGVs that never failed inspection: they are likely to be newer, with low to moderate mileage, adequate maintenance, and electronically managed engines. (Some, but not all, could be recruited instead from reputable fleets participating in federal or California funded emissions studies.) The vehicles from used truck dealerships correspond to the LDGVs with failures in their inspection records: they will constitute a mixed fleet, including older and newer vehicles, in various states of repair, with both mechanical and electronic injection.

Our recruitment criteria for heavy-duty vehicles do not map directly onto categories in the general vehicle population as those for light duty vehicles did. It will consequently be more difficult to determine the weightings of test data that best represent the vehicle mix in the general population. It will be necessary to consider the mix of vehicle miles traveled in the region by each weight grouping, which can be estimated from registration records and TIUS/VIUS data.

The sample numbers in recommendation 1 represent engineering judgments, and do not result from formal statistical analyses of sampling errors and their propagation through the CMB (Appendix F). As implemented, the program recommended here will reflect ongoing decisions about the test cycles and operating modes to be used for vehicle emissions measurements, the analytical methods to be used to determine the chemical constituents of samples, the selection and method for compositing samples, and technical issues such as collinearity assessment in the CMB analysis. Although all of these decisions will make use of the knowledge gained from

previous CMB analyses, the final database and the CMB models in the proposed apportionment study will nonetheless be substantially different from those now available. Hence, existing data and CMB analyses cannot be used to provide estimates of the sampling errors that are likely to be achieved in the proposed apportionment study. The numbers of vehicles recommended in 1a and 1b represent a reasoned compromise of vehicle procurement constraints and statistical representation for the groups of vehicles identified.

The recommended sample numbers should suffice to cover the range of chemical variations found in real-world vehicle exhaust. The effective dimensionality of the overall vehicle source matrix is much lower than the number of measured chemical species (Appendices C,D), and will probably remain under ten even with the enhanced speciation and analytic precision recommended below. [To a first approximation, there are only three feedstocks (gasoline, diesel fuel, and lubricating oil). Gasoline emissions primarily reflect combustion stoichiometry (lean *vs.* rich) and exhaust treatment (no catalyst, oxidizing catalyst, or oxidizing/reducing catalyst). Diesel technologies are similarly limited in number (two-stroke *vs.* four-stroke power cycle, natural *vs.* turbocharged aspiration, and electronic *vs.* mechanical management of fuel injection).]

The proposal to recruit fewer diesel than gasoline vehicles does not rest on any presupposition that gasoline exhaust contributes a larger fraction of ambient PM or is more diverse in composition. This recommendation simply acknowledges the greater difficulty of recruiting and testing heavy duty diesels, together with the more limited extent of existing data on their exhaust composition and its dependence on vehicle technology and operation. It appears cost-effective to explore the determinants of diesel exhaust composition at this stage, and to defer larger vehicle surveys until they can be guided by improved understanding of these determinants.

***2. Minimize the physical aggregation of exhaust samples from different vehicles. If needed to assure adequate analytic sensitivity, add extra ports to the exhaust tunnel to draw multiple sample streams from the same test run. If resource limits require consolidation of samples, pool those most likely to be similar to each other.***

This recommendation addresses two distinct objectives. The first is the need to consolidate vehicle test data into composite profiles that represent the Los Angeles population rather than the sample fleet. As noted above and illustrated in Appendix B, the elimination of biases in vehicle recruitment will require the differential weighting of test data from different vehicle groups. Physical aggregation before sample analysis would foreclose this possibility, and recommendation 2 is thus a concomitant of recommendation 1. The second reason to distinguish among individual vehicles is to provide for accurate estimates of statistical uncertainty. The uncertainty in composite profiles will depend on the scatter in individual test results and its origins in measurement error, environmental fluctuations, and vehicle differences.

Recommendations 1 and 2 discuss sampling and sample handling in terms of vehicles, and do not explicitly address test cycles and operating modes. Whether to distinguish operating

modes in vehicle testing is a decision left to those with more specific expertise in this area. The recommended measurement campaign will be able to exploit new test cycles that have been specifically designed to represent current real-world operation in the study region. On the one hand, the improved cycles should lessen the need to extract from CMB analyses an independent estimate for the real-world mix of operating modes. Dropping unneeded distinctions between emissions conserves measurement resources, and can improve the numerical stability of CMB estimates for the categories that remain. On the other hand, test cycles that capture the 24h mix of operating modes across the entire basin may poorly represent conditions relevant to some of the vehicle-rich environments recommended below for ambient sampling. The benefits of distinguishing operating modes may also differ between gasoline and diesel vehicles, given the greater diversity of stereotypical operations associated with HDDVs (e.g. municipal garbage trucks vs. long-haul tractors).

**3. Investigate interfering sources.** *Obtain exploratory samples from non-road diesels that use heavier grades of fuel, including railroad locomotives and coastal shipping.*

The Caltech group estimates that on-road diesel exhaust accounted for only about 50% of the basin-wide EC emissions in Los Angeles during their study year (Gray and Cass, 1998). If the carbonaceous portion of non-road diesel exhaust is well represented by the on-road diesel profile, then a CMB estimate for ambient diesel exhaust can be interpreted as an undetermined mix of non-road and on-road emissions. If non-road diesel exhaust should instead prove chemically dissimilar, then CMB analyses will need to be (a) restricted to ambient samples presumed free of non-road emissions, or (b) preceded by an adjustment of the ambient data to remove the independently estimated non-road contribution, or (c) augmented to include a separate profile for non-road diesels.

**4. Include markers for major non-vehicular sources in the chemical analysis of exhaust and ambient samples.**

The Caltech group estimates that primary gasoline and diesel exhaust together accounted for substantially less of their measured organic PM in Pasadena than did meat cooking and wood burning, and only twice as much as these activities in downtown Los Angeles (Schauer et al., 1996). It will thus be necessary not only to distinguish diesel from gasoline emissions, but also to disentangle both from the organic material contributed by meat cooking and wood burning. This will require accounting for the latter contributions in the CMB, but non-vehicular source testing lies outside the scope of the experimental program now under consideration.

Since the composition of emissions from meat cooking and wood burning is expected to be relatively uniform over space and time, existing Caltech and NFRAQS profiles can be employed to represent these emissions in the CMB analysis. However, the existing profiles do not benefit from the integration of Caltech and NFRAQS analytical methods called for in the next two recommendations. Recommendation 4 preserves the possibility of revisiting the CMB analysis if the enhanced measurements should ever be extended to non-vehicular sources. In the

meantime, the incommensurate profiles from Caltech and NFRAQS are likely to yield somewhat differing CMB estimates for the split between vehicular and other contributions to ambient PM.

***5. Involve advocates of both the Caltech and NFRAQS approaches in experimental design, sample collection, and laboratory analysis.*** *Work with participants to eliminate unnecessary duplication of effort, but allow for redundant measurements where these will illuminate issues of interpretation. Consider engaging an independent coordinator to promote communication and draft sample- and data-sharing protocols for the participants' review.*

This is not a recommendation for a 'shoot-out', or competition, where collocated measurements are compared against standards to determine which are most accurate. It is, rather, a recommendation to exploit the extended chemical resolution that can be obtained by combining the best of different sampling and analysis methods. By increasing the number of compounds specific to certain source types, and by using the most sensitive analyses available for each one, such an integrated measurement program will provide the CMB with increased power to distinguish the contributions of different source categories.

An important ancillary benefit of collaborative measurements is that they will make possible an improved understanding of previous studies. The Caltech and NFRAQS studies yielded markedly different apportionments. The difference may reflect the 1.5 decade span between the study years and the geographic and climatologic distance between the study areas, but it may also reflect the substantial differences between the species and sources examined in the two CMBs. Each study relied for some important sources on chemical markers that were not measured in the other study, rendering their profiles for these sources essentially incommensurable. The combined measurements recommended here will provide extended profiles that can be compared with those from each of the earlier studies.

***6. Employ both the NIOSH and IMPROVE methods for all EC determinations.***

"Elemental" carbon is the most influential single species in CMB analyses of the gasoline/diesel split. It is defined operationally, as the result of a measurement protocol, rather than fundamentally, in terms of its physical characteristics or molecular composition. The EC/total carbon fractions returned by the NIOSH protocol appear to exhibit sharper differences between diesel exhaust and other carbonaceous emissions (Appendix E), offering advantages in terms of source discrimination. On the other hand, more historical data have been obtained with the IMPROVE protocol, and the relationship of these determinations to atmospheric visibility has been more extensively studied. Recommendation 6 will provide the data needed to bridge different measurement programs and apportionment studies.

***7. Collect ambient samples in a variety of vehicle-rich environments.*** *At a stationary sampling platform in downtown Los Angeles, collect diurnally resolved (2 to 4 per day) ambient air samples for at least one month. Use additional roadside or mobile sampling platforms to collect roadway air samples representing diverse mixes of vehicles and operating conditions.*

Recommendation 7 reflects the focus on vehicle exhaust in the projected source characterization program. Its intent is to minimize contributions to the CMB from poorly characterized sources such as non-road diesel exhaust and photochemical reaction, as well as incompletely characterized sources such as meat cooking and wood burning. Downtown Los Angeles is recommended as a population-oriented site that Caltech found to be heavily influenced by vehicle exhaust in 1982. The diurnal resolution at this platform should be chosen to isolate the fresh emissions from morning rush hour, minimally contaminated by the products of secondary photochemistry. Samples can also be collected at sites more affected by non-vehicular sources, but these may require an expanded source testing program to be properly interpreted by CMB analyses, as discussed under recommendation 4.

Sampling in a variety of roadway environments is recommended to provide data with which to exercise the CMB. Vehicle-dominated samples can be used to test the response of CMB results to qualitative perturbations from more typical ambient mixes of source contributions. (The source perturbations are not quantifiable without the ventilation data that would be needed to characterize the relative contributions of the ambient background.) Appropriate responses can build confidence in the overall analysis, while inappropriate responses can of course suggest areas needing attention. Diversity in the LDGV/HDDV mix can be sought in such perturbations as the weekend drop in HDDV traffic, geographic restrictions on HDDV traffic (e.g. some freeways), and dedicated facilities (e.g. bus terminals). Diversity in operating modes can similarly be sought from different traffic conditions (stop and go vs. free flowing), different roadways (surface street vs. freeway), and different grades (to which heavy-duty vehicles are particularly sensitive). Even differences in vehicle condition might be found, in different socioeconomic neighborhoods.

***8. Involve advocates of both the Caltech and NFRAQS approaches in data interpretation, and provide opportunity and time for them to interact and reconcile results. Support the development of a common electronic data base formatted to facilitate the exploration of alternative solutions to the CMB.***

Recommendation 8 is intended to promote a shared understanding of the assumptions and ambiguities in the final CMB analyses. An attractive path toward this objective is to create a computer environment that enables each individual researcher to interactively explore the effects of his own decisions and hypotheses on the CMB solution. A collaborative map of the physically plausible interpretations emerging from this exploration then serves as a meaningful characterization of uncertainty.

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**Appendices**

- A. Statistical issues, R.F. Gunst 7/5/00.
- B. Homogeneity of vehicle exhaust, W.H. White 7/27/00.
- C. Dimensions of variation in vehicle exhaust, W.H. White 9/24/00
- D. Types of uncertainty in CMB estimates, W.H. White 8/22/00
- E. Measurement of EC, W.H. White (10/31/00)
- F. Statistical fleet-sizing, R.F. Gunst (10/24/00)

## **Appendix A: Statistical Analysis of Vehicle Populations to be Considered for Emission Inventory Studies**

Richard F. Gunst, 7/5/00

### *Statistical Issues*

This document summarizes an initial perspective on recent fine particulate mass source apportionment studies. It is hoped that this perspective will foster additional conversation concerning statistical issues of the proposed Southern California gasoline/diesel exhaust particulate apportionment study. The issues raised in this report are intended to focus on matters that affect the use of chemical mass-balance receptor modeling to apportion source contributions from chemical species measurements. It is not the intent of this report to critique either past measurements or previous analytical efforts. The documents that were received and used to form this perspective indicate that the investigators in these studies are highly competent scientists using the latest technological advances and very sophisticated statistical methods. Rather, it is hoped that the perspective contained in this report will highlight the need for additional thoughtful consideration of statistical concerns in the planning of the proposed apportionment study of these complex environmental processes.

Central to the discussions below are the apportionment study performed by researchers from California Institute of Technology (Schauer et al. 1996) and the apportionment study of the Northern Front Range Air Quality Study (Watson, et al. 1998). These studies are referred to below as the CalTech and the NFRAQS studies, respectively.

Striking differences in conclusions resulted from the CalTech and the NRFAQS studies. For example, the CalTech study concluded that vehicle emissions accounted for approximately 35-56% of the fine organic aerosol concentrations, with diesel emissions contributing up to five times more than gasoline vehicle emissions. Fine total particle concentrations (elemental carbon and organic carbon) were caused by a large number of emissions sources, with diesel and gasoline emissions contributing in much lower percentages. Again, diesel emissions contributed a much greater percentage of the particulate concentration than gasoline vehicles.

On the other hand, the NFRAQS study concluded that the Denver area urban contributions to  $PM_{2.5}$  carbon mass were 85% due to vehicle exhaust. The contribution of light-duty gasoline vehicles to the  $PM_{2.5}$  carbon mass was estimated to be 2.5 to 3 times that of diesel vehicles.

These differing conclusions are likely due to a number of factors, not a single feature of either study. Like the apportionment studies themselves, it would be difficult to determine the contributions of the various factors. This is in part because a number of scientific decisions were made in each study that led to differences in implementing the data collection and modeling components of the chemical mass balance receptor modeling approaches in the respective studies. No attempt is made to enumerate all these differences or to resolve them. Nevertheless, by highlighting some of the key differences that likely affected the statistical results, these differences can be considered in the planning for the proposed Southern California apportionment study.

### ***Data Collection***

The CalTech apportionment study used ambient fine particulate measurements that were collected at 4 sites in the Southern California basin in 1982 (Schauer et al. 1996). Elemental carbon, organic carbon, and a few trace elements were measured at these sites and for potential source contributors. Measurement of trace elements such as elemental carbon permitted distinct source profiles to be constructed for some of the emissions sources. Source emissions measurements were obtained from sites located within an 80 x 80 km. grid centered over Los Angeles.

Diesel truck emissions from data collected in 1982 (Gray et al. 1986) and a newer fleet of two late-model, low-mileage diesel trucks analyzed in Hildemann et al. (1991) are acknowledged to have similar organic compound concentrations but much different elemental carbon concentrations. The analysis of Schauer et al. (1996) combined the elemental carbon emission rate of Gray et al. (1986) with the organic carbon emission rates of the later Hildemann et al. (1991) study in the source profiles.

The NFRAQS measurements were taken during the winters of 1996 and 1997 and the summer of 1996 at 9 sites in the Denver urban region. Some ambient and source emissions measurements were taken as part of NFRAQS and some were acquired through existing monitoring networks. Extensive measurements of mass, chemical elements, ions, organic and elemental carbon, organic compounds, and carbon-14 abundances were obtained.

Vehicle emissions characterizations were obtained from a fleet of 111 vehicles (76 cars and 35 trucks) in the summer of 1996 and 84 vehicles (58 cars and 26 trucks) in the winter of 1997. Each light-duty vehicle was tested using the FTP test protocol, with both composite and

individual phase (bag) emissions included in the analyses. Heavy-duty diesel trucks were tested using one of three driving cycles: the Central Business District, Heavy-Duty Truck Transient, and West Virginia Truck cycles. Model years ranged from 1971 to 1996.

### *Statistical Issues*

#### *Over a Decade Between the Two Studies*

CalTech: 1982: older technology vehicles, leaded fuels

NFRAQS: 1996: mixture of vehicle technologies and emissions control systems; unleaded fuels, different blends for winter and summer

Measurement technology changes

#### *Two Markedly Different Locales*

CalTech: low altitude, coastal

NFRAQS: high altitude

Regional Weighting: urban vs. rural

#### *Fleet Selection*

CalTech: small fleet, only 2 trucks; pre-LEV technology

NFRAQS: large fleet, mixture of vehicle technologies and vehicle control systems, different heavy-duty truck testing cycles

#### *Wood Burning and Meat Cooking*

Selection of wood types, meats

### *Source Profiles*

Cass et al. (1982) report that atmospheric carbon particulate emissions are generated from more than 70 sources. Chemical mass balance equations are stable for only a maximum of about a dozen sources. The CalTech apportionment study includes 15 potential sources, with only 12 used in the calculations. Concentrations of 100 organic compounds were obtained for both source and ambient receptor samples, as well as for a few trace elements. A total of 48 of these measurements were used in the chemical mass balance equations.

A chemical compound was used in the mass balance equations in the CalTech study only if the area-wide emissions total for the compound from the examined sources was approximately equal

to the ambient concentrations measured at the 4 sites. Approximate equivalence was established by comparison with concentrations of relatively inert fine elemental carbon, fine silicon, and fine aluminum.

The NFRAQS study uses at most 11 emissions sources in any analysis. The motor vehicle source categories were partitioned into light- and heavy-duty diesel exhaust emissions and three-categories of light-duty gasoline vehicle exhaust emissions: hot stabilized operation, cold starts, and high particle emitters. A total of 80-85 chemical species were measured and used in the chemical mass balance equations. Source profiles were normalized to reconstructed mass rather than measured mass because the two “often differed significantly” (Watson et al. 1998, p. 4-12).

### *Statistical Issues*

#### *Selection of Potential Source Contributors*

Different studies can be expected to produce similar results only if they begin with the same selection of potential emissions sources. It is well known and understood that serious biases can result if contributing emissions sources are not included in the chemical mass balance equations. In addition, if the partitioning of sources (e.g., composite emissions into phase emissions) were to result in the elimination of other sources or source profiles because of the introduction of collinearities, interpretation of source contributions would be problematic.

#### *Selection of Chemical Species*

Exclusion of potentially important chemical species, including tracer elements, can result in the exclusion of emissions sources because of the inability to formulate noncollinear source profiles.

*Both Studies:* Important chemical species may differ by locale and over time.

Individual decisions were made to eliminate collinearities.

*CalTech:* Equivalence of ambient and source chemical compounds. Averaging individual source profiles to represent source categories.

*NFRAQS:* Normalize source profiles to estimated particle mass, not measured mass. Eliminating source profiles when attributed mass sufficiently differs from measured mass. Negative attributions set to half the uncertainty.

Selecting an individual species profile to represent source categories.

#### *Fleet Selection*

*CalTech:* small fleet, only 2 trucks; pre-LEV technology

NFRAQS: large fleet, mixture of vehicle technologies and vehicle control systems, different heavy-duty truck testing cycles

#### *Wood Burning and Meat Cooking*

These are necessary but severe limitations on the use of chemical mass balance equations. The addition of tracer elements is intended to alleviate some collinearity problems by providing better identification of some sources but subjective decisions were required to eliminate other collinearities.

#### *Estimation Methods*

The chemical mass balance receptor modeling approach to the apportionment of carbon-based particulate sources is a specialized version of a general statistical methodology that is often referred to as *measurement error modeling* (e.g., Fuller 1987) or *errors-in-variables modeling*. The *effective variance solution* of the chemical mass balance estimating equations is an adaptation of Gauss-Newton approximation to the solution of nonlinear measurement error modeling equations presented by Britt and Luecke (1993; see also Fuller 1987, Section 3.2). Both the CalTech and the NFRAQS source apportionment studies use EPA/DRI software to solve the chemical mass balance equations.

#### *Statistical Issues*

##### *Chemical Species Add Linearly*

The linearity assumption is one of convenience that may be approximately true. Theoretical advances no longer make this assumption necessary for calculation of solutions to the mass balance equations or for the calculation of uncertainty limits.

##### *Measurement Errors are Uncorrelated*

This too is an assumption of convenience. It is very likely not a valid assumption since many of the chemical species measurement are taken at the simultaneously time with the same instrumentation. Britt and Luecke's (1973) solution does not require this assumption.

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## Appendix B: Homogeneity of vehicle exhaust

Warren H. White, 7/27/00

The objective given by the Statement of Work for CRC/NREL project E-59-1a is “to provide a recommendation regarding the sample size of vehicles to be tested on chassis dynamometers as part of a proposed gasoline/diesel exhaust particulate matter (PM) apportionment study in Los Angeles.” It is understood that the analytical framework of the apportionment study will be supplied by chemical mass balance (CMB) analysis, as exemplified in prior studies by Schauer et al. (1996) and Watson et al. (1998).

In simple terms, the size required for the vehicle sample will turn on the chemical homogeneity of vehicle exhaust, the accuracy with which exhaust can be considered to be a chemical ‘compound’, of fixed composition. (Measurement imprecision can be addressed without increasing the vehicle sample, through repeat testing of the same vehicles.) More precisely, the required sample size will depend on the homogeneity of exhaust within identifiable categories of vehicles (e.g. diesel, catalyst-equipped gasoline, pre-catalyst gasoline) and/or operating conditions (e.g. cold start, hot stabilized operation, off-cycle operation).

At the present time, the chassis dynamometer tests carried out during NFRAQS (Watson et al., 1998) appear to be the only data available that show the variability of exhaust from superficially similar vehicles sampled from a common location during a common time period. This note reviews the homogeneity of the NFRAQS exhaust data in the context of their use for CMB analysis. The data are presented in a format intended to promote direct and intuitive evaluation, with a minimum of theoretical assumptions and statistical manipulations. Although the NFRAQS data considered here are specific to Denver in winter 1997, the qualitative chemical variability they exhibit may relate to current conditions in Los Angeles as well.<sup>1</sup>

We begin with a conceptual review of the CMB approach. Figure 1 sketches vehicle-test data for a simplistic application where all sources of emissions fall into one of two categories. The test results in the left-hand plot are favorable to CMB analysis because they indicate that each source category has a characteristic, and distinct, exhaust composition. The ratio of marker to total carbon from category A vehicles is the same for high-emitters (high g/mi TC) and low

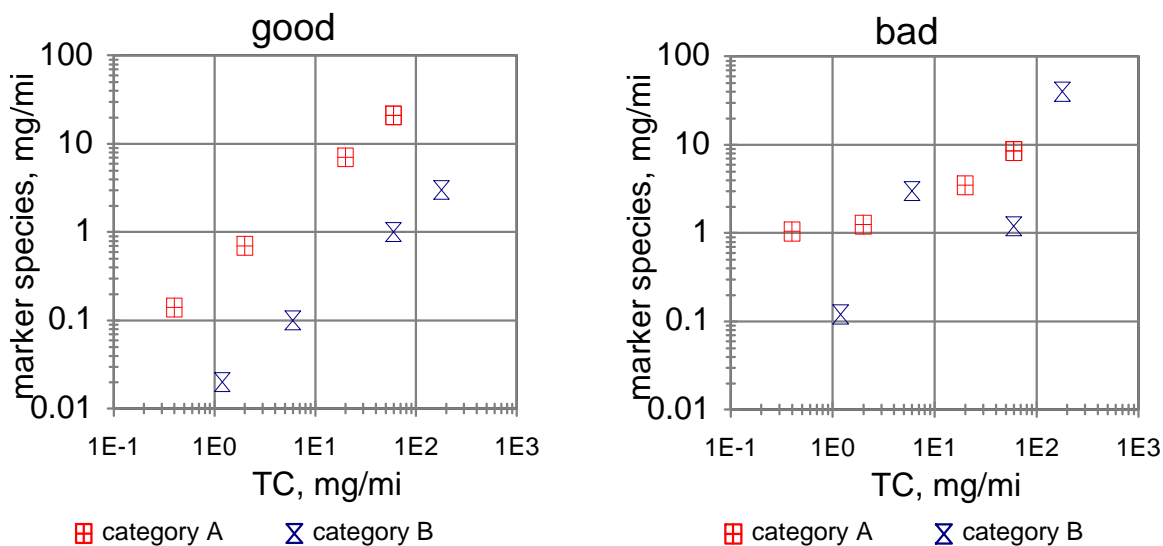
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1. It should be noted, however, that NFRAQS found large differences in light duty vehicle exhaust between the winter tests examined here and a similar program of testing during summer 1996 (Cadle et al., 1999).

emitters (low g/mi TC), and is consistently greater than the ratio for category B vehicles. If we know A and B to be the only categories emitting carbon and the marker species, then only simple algebra is required to determine their contributions to the carbon in a measured sample of ambient air:

$$[TC_A]_{air} = \{[M]_{air} - [TC]_{air}(M/TC)_B\} / \{(M/TC)_A - (M/TC)_B\}, \quad [1a]$$

$$[TC_B]_{air} = \{[M]_{air} - [TC]_{air}(M/TC)_A\} / \{(M/TC)_B - (M/TC)_A\}. \quad [1b]$$

Here  $[M]_{air}$  and  $[TC]_{air}$  are the measured ambient concentrations of marker and total carbon,  $(M/TC)_A$  and  $(M/TC)_B$  are the ‘signature’ ratios measured in exhaust, and  $[TC_A]_{air}$  and  $[TC_B]_{air}$  are the desired source attributions.



**Figure 1.** Idealized examples of emissions-test results. Each symbol represents an individual measurement sample (e.g. of a large truck or a homogeneous group of cars), from one of several source categories (e.g. heavy duty diesels or visibly smoking gasoline vehicles). The plots show hypothetical relationships between emission rates for source-specific marker species and total carbon (TC). Logarithmic axes are used to facilitate the consideration of vehicles with widely differing emissions rates.

An attractive feature of the CMB solution [1a,b] is that it does not involve absolute rates (g/hour) of TC emissions. In place of source terms summing [emissions/vehicle-mile]x[vehicle-miles traveled] over all types of vehicles, CMB analysis substitutes the detailed chemical speciation of emissions and ambient air. A major potential benefit of this trade-off is that individual sources of widely differing magnitudes (in terms of mg/mi TC) can have chemically

similar emissions (in terms of dimensionless M/TC). We can then settle for chemically characterizing a limited sample of ‘representative’ sources, without having to estimate mass emission rates throughout the population. The other side of the trade-off is that it becomes necessary to identify and characterize these chemical ‘signatures’. Usable marker species exist only if we can partition sources into chemically homogeneous categories.

Figure 1's right-hand plot illustrates two ways in which actual test results can depart from the theoretical assumptions of CMB analysis. In category A, species emissions correlate perfectly ( $r^2 = 1.0$ ) with TC emissions, but the ratio  $M_A/TC_A$  varies systematically with the rate. The ratio  $M_B/TC_B$  for category B shows no such trend, and reflects a strong correlation ( $r^2 = 0.9$ ) between species and TC emissions, but nevertheless varies within the category. Both situations present the analyst with the need to determine composite source profiles, chemical signatures that apply to categories in the aggregate and may only approximately represent any individual source. Figure 2 illustrates some alternative approaches to this problem.

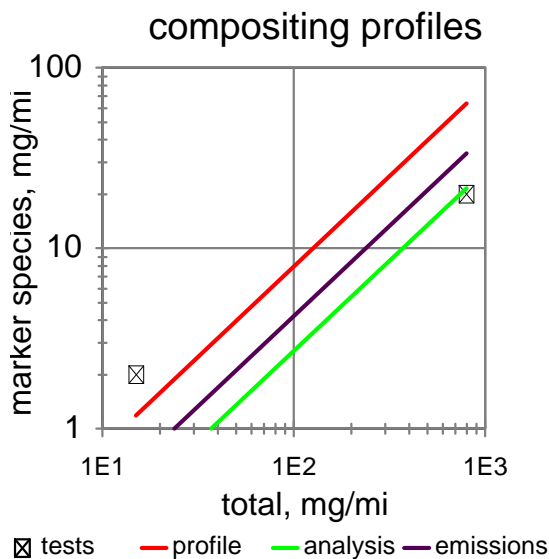


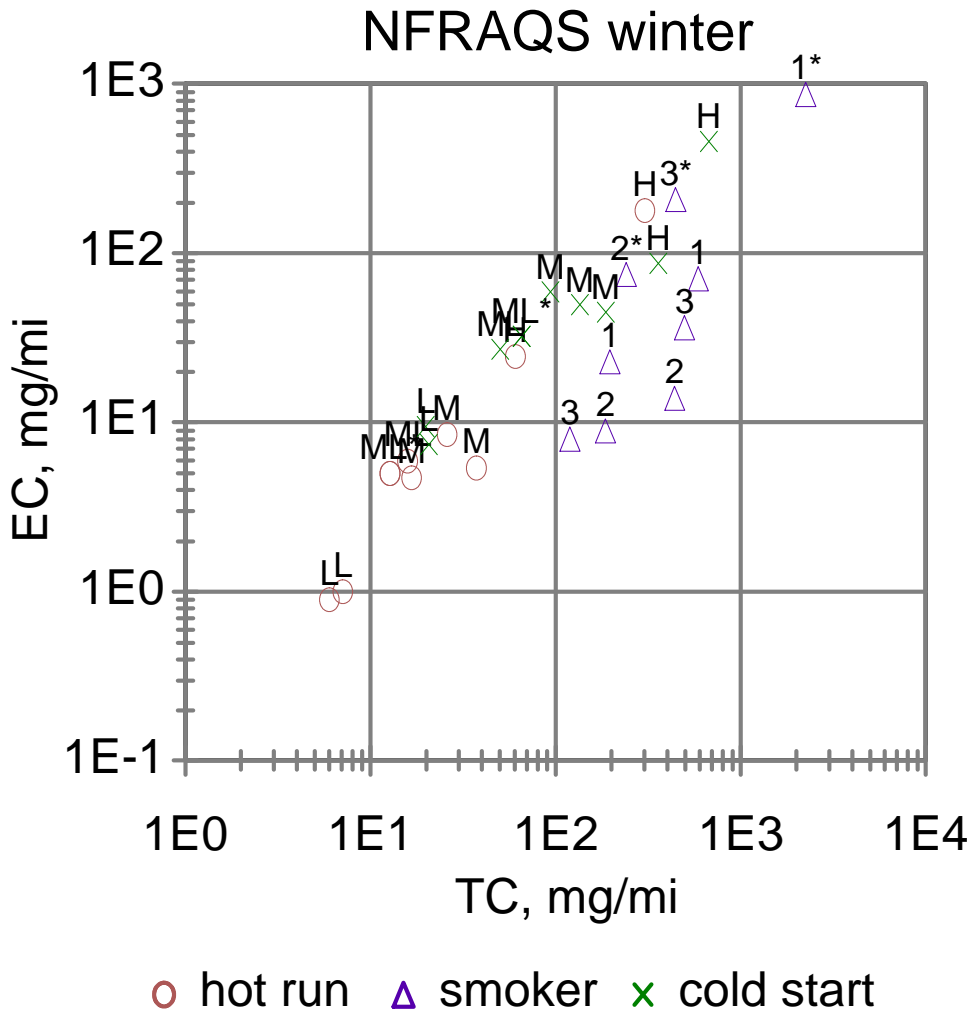
Figure 2. Hypothetical emissions data from two vehicle tests (symbols), with three possible chemical signatures for the aggregate vehicle class. Physically pooling the test samples before chemical analysis yields the lowest sloping line (‘analysis’); this represents the ratio  $M/TC = ([M]_1 + [M]_2)/([TC]_1 + [TC]_2)$ , where  $[*]_1$  and  $[*]_2$  are the samples from the two

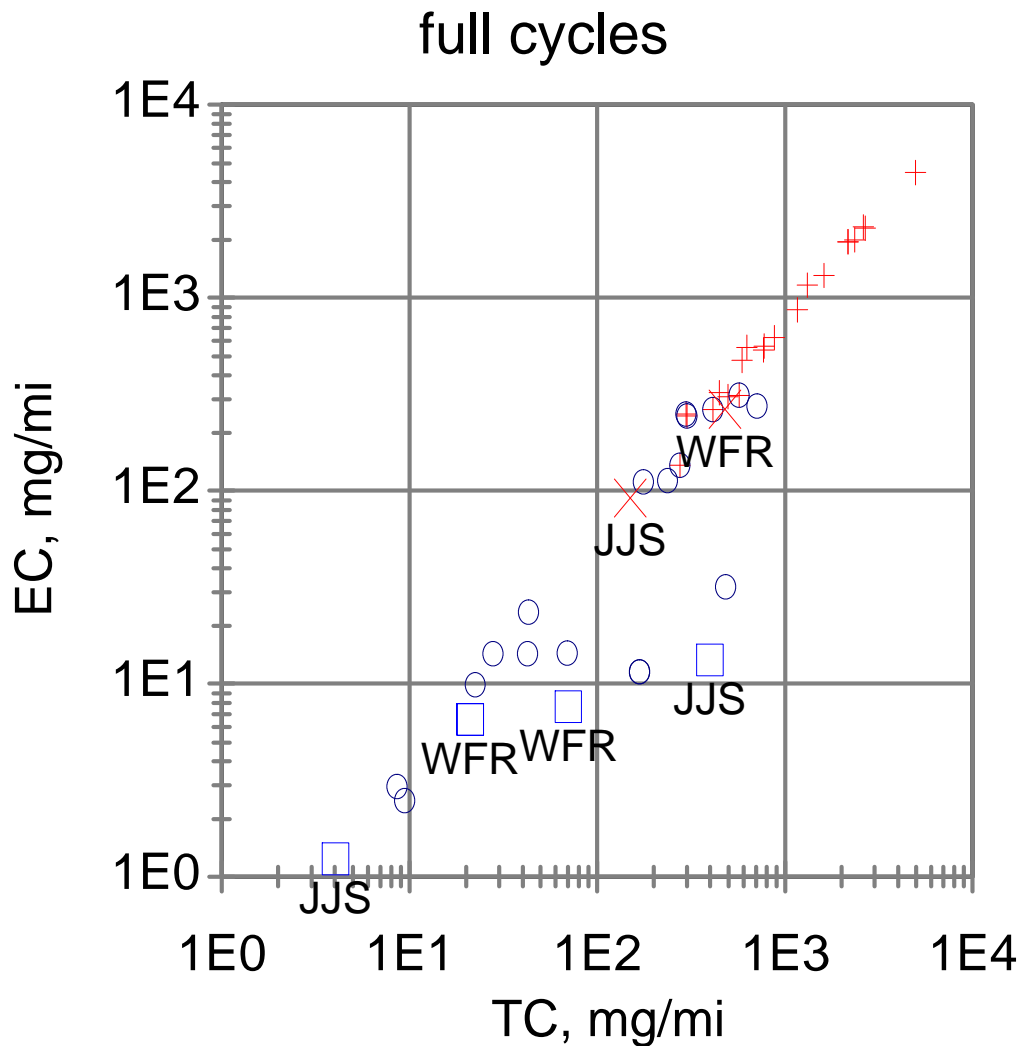
tests. Numerically averaging the emissions profiles after chemical analysis yields the highest sloping line ('profile'); this represents the mean  $([M]_1/[TC]_1 + [M]_2/[TC]_2)/2$  of the ratios from the individual tests. The middle sloping line ('emissions') indicates the ratio  $Q_M/Q_{TC}$  of aggregate emissions for the category as a whole, if low emitters (lower-left symbol) outnumber high emitters (upper-right symbol) by 10:1 in terms of vehicle-miles traveled.

Figure 2 shows that the key parameters  $(M/TC)_A$  and  $(M/TC)_B$  in the CMB solution [1a,b] can be sensitive to our accounting procedures when we work with chemically inhomogeneous source categories like those in the right-hand plot of Figure 1. If the vehicle category tested in Figure 2 were the source of all species M in the atmosphere, then we would estimate this category's contribution to total ambient carbon by determining the intersection in Figure 2 of the horizontal line representing the ambient concentration of M with the sloping line representing the source ratio M/TC. The horizontal coordinate of this intersection, which represents the total ambient carbon attributed to the tested source, varies by a factor of about 3 across our alternative source signatures.

DRI composited their exhaust samples both physically and numerically to arrive at source signatures for the NFRAQS CMB. The roughly 125 exhaust samples collected from individual light-duty (LD) vehicles were first sorted, by fuel type, phase of test cycle, and observed mass emissions, into about 50 different subgroups of comparable vehicles and operating conditions. The samples within each subgroup were physically pooled, then chemically analyzed. Another 15 exhaust samples from heavy-duty (HD) diesel trucks were analyzed separately. The resulting chemical profiles (normalized by reconstructed total mass rather than the total carbon used here) were then examined for similarities and differences. After some experimentation, the roughly 65 different exhaust profiles were eventually partitioned into four relatively homogeneous categories: gasoline cold starts (FTP phase 1 for non-smoking LD vehicles), gasoline hot-stabilized operation (FTP phase 2 for non-smoking LD vehicles), gasoline smokers (FTP phases 1-3 for visibly smoking LD vehicles), and diesels (the full LD FTP or HD truck cycle). Within each of these categories the individual profiles were averaged numerically, to yield the four distinct composite exhaust profiles that were ultimately used in the CMB analysis.

Figures 3 - 12 below plot NFRAQS (and a few Caltech) results in the format of Figures 1 and 2, providing a visual indication of the apportionment uncertainties introduced by chemical heterogeneity. To allow the reader to form his or her own impressions without prejudice, these figures are presented without editorial commentary.





+ DRI diesel   o DRI light   x CIT diesel   □ CIT light

**Figure 4.** Full-cycle elemental carbon (EC) and total carbon (TC) emissions measured in tests of light- and heavy-duty gasoline and diesel vehicles. DRI data are from the NFRAQS winter measurements (Fujita, 2000). In addition to the light-duty gasoline vehicles represented in Figure 3, they include 5 light-duty and 15 heavy duty diesel vehicles. CIT (Caltech) data are from measurements reported by Rogge et al. 1993 (WFR) and Schauer 1998 (JJS). Rogge et al. and Schauer each pooled samples from three different vehicle categories, collected in Los Angeles in different years: catalyst-equipped light-duty gasoline vehicles, pre-catalyst light-duty gasoline vehicles, and heavy-duty (WFR) or medium-duty (JJS) diesel trucks.

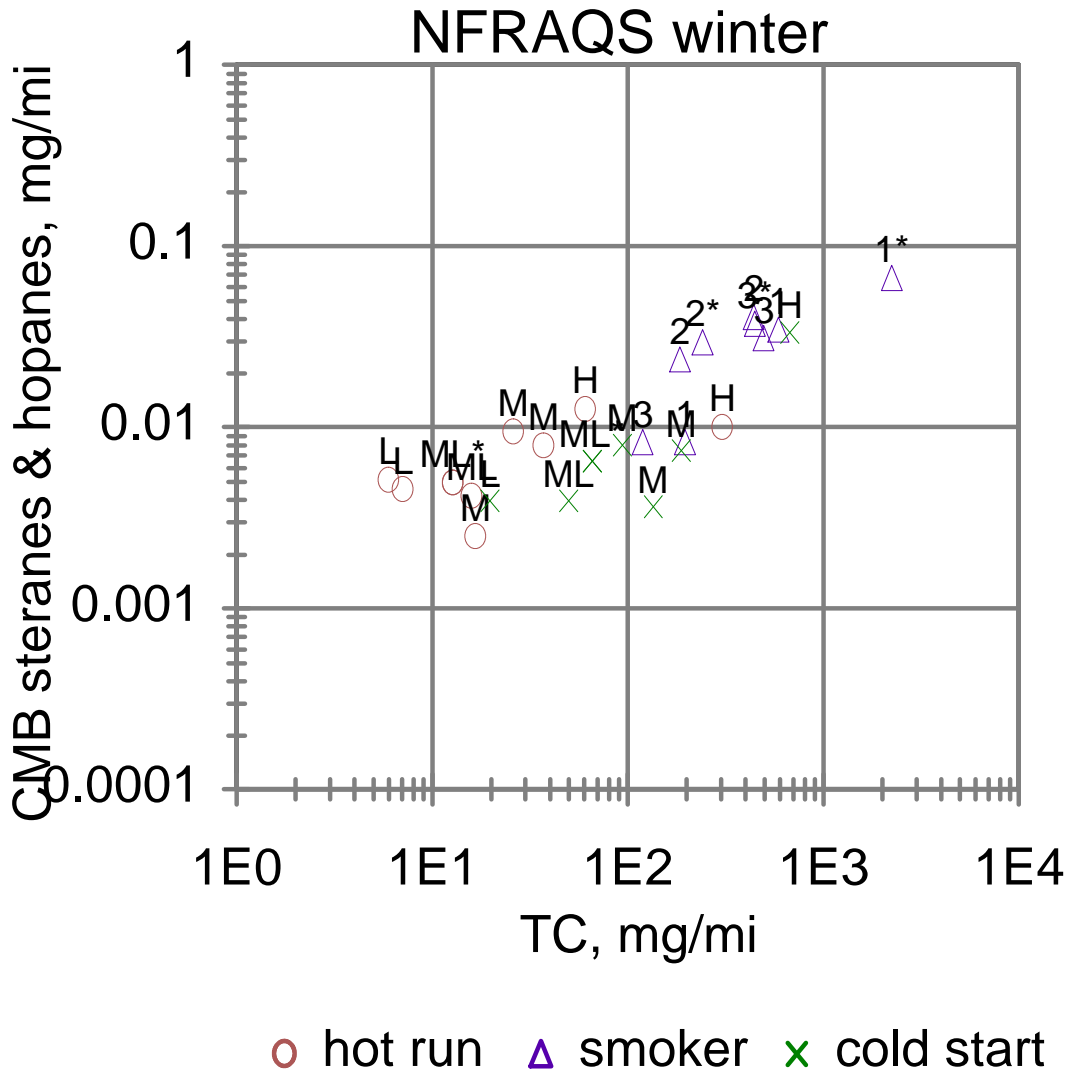


Figure 5. Hopane and sterane emissions measured in pooled exhaust samples from light-duty gasoline vehicles. The vertical coordinate shows the sum of the individual hopanes and steranes included as fitting species in the final NFRAQS CMB. Format and data source are otherwise as in Figure 3.

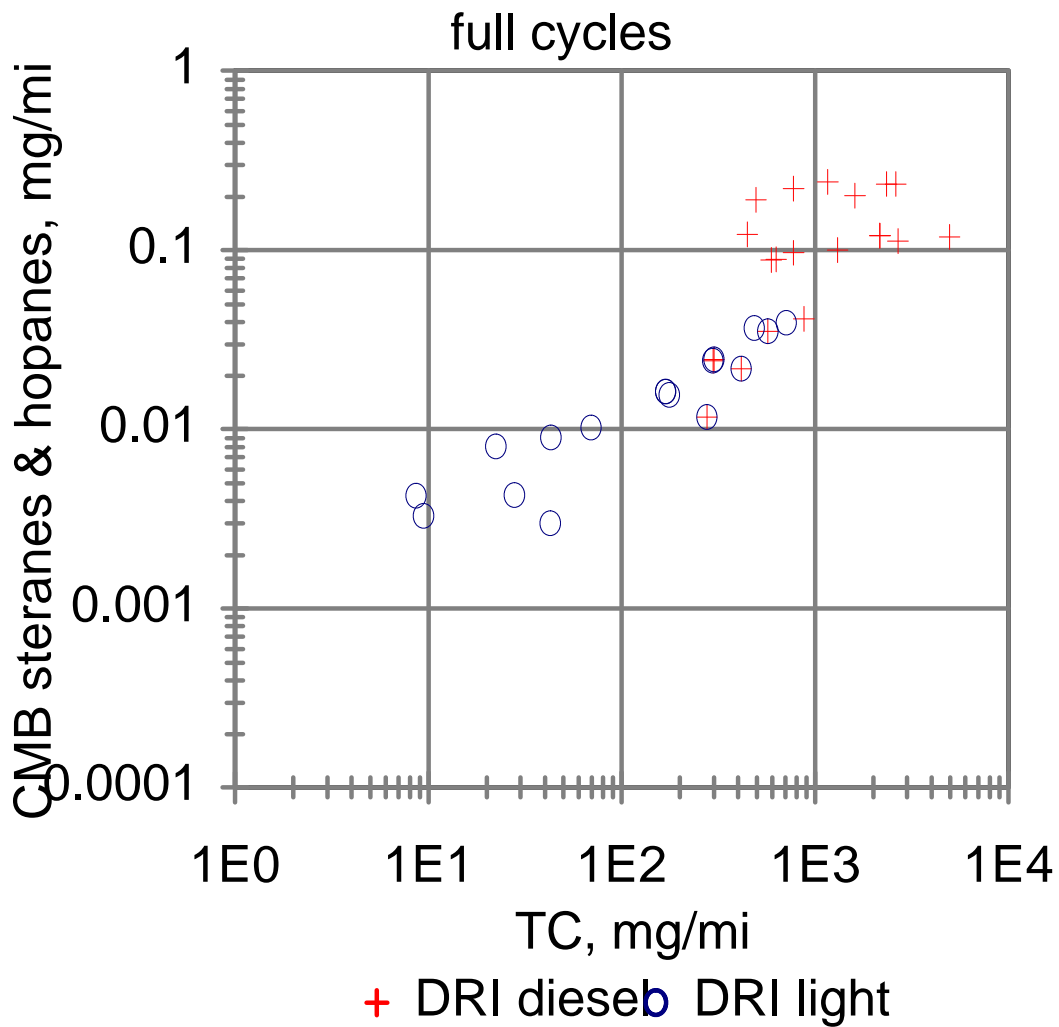


Figure 6. Full-cycle emissions of hopane and steranes measured in tests of light- and heavy-duty gasoline and diesel vehicles. The vertical coordinate shows the sum of the individual hopanes and steranes included as fitting species in the final NFRAQS CMB. Format and data source are otherwise as in Figure 4.

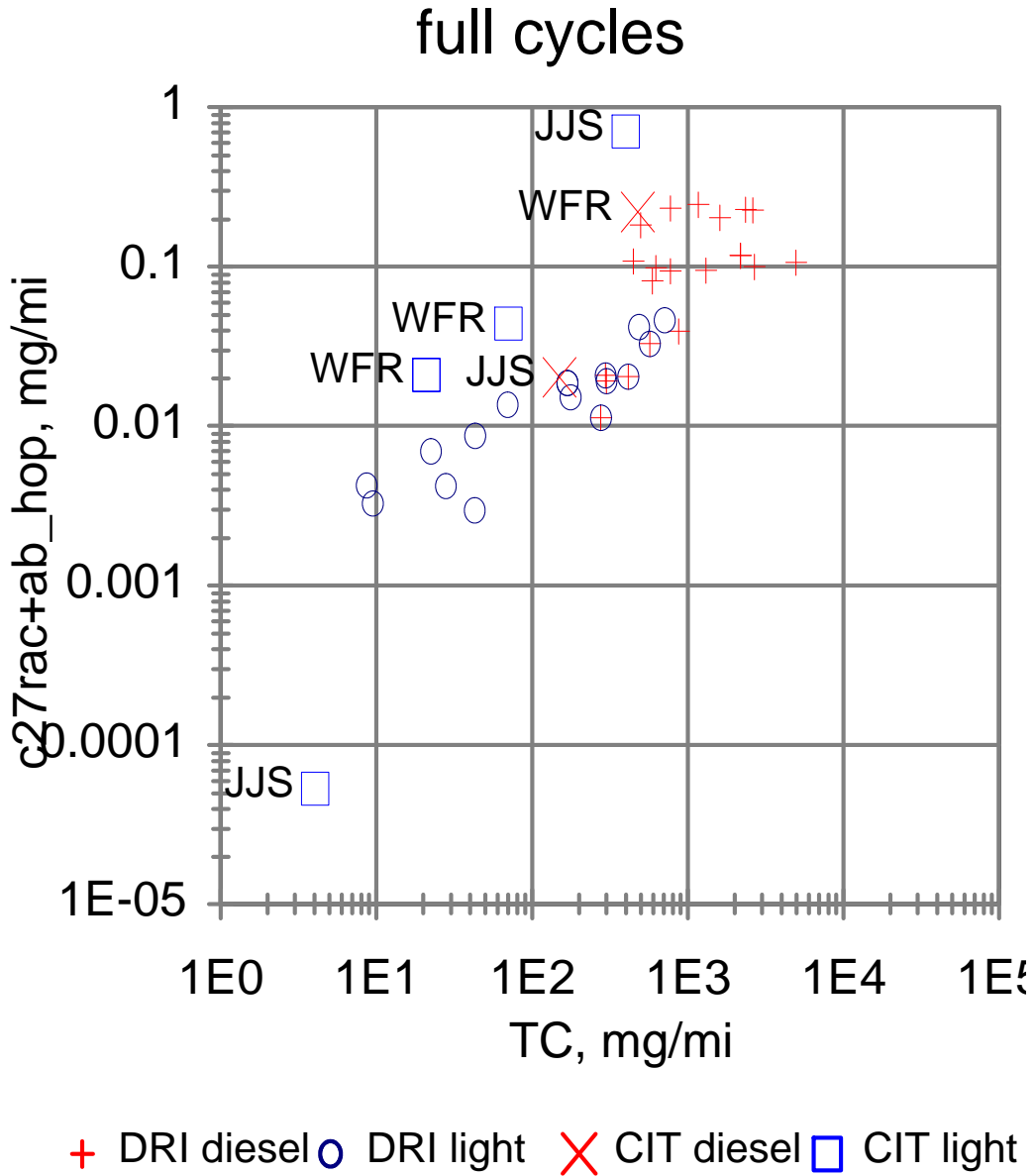


Figure 7. Full-cycle emissions of (20R)-5*a*(H),14*a*(H),17*a*(H)-cholestane ('c27rac') and 17*a*(H),21*β*(H)-hopane ('ab\_hop') measured in tests of light- and heavy-duty gasoline and diesel vehicles. The plotted sterane and hopane were included in both the DRI and CIT measurements. Format and data sources are otherwise as in Figure 4.

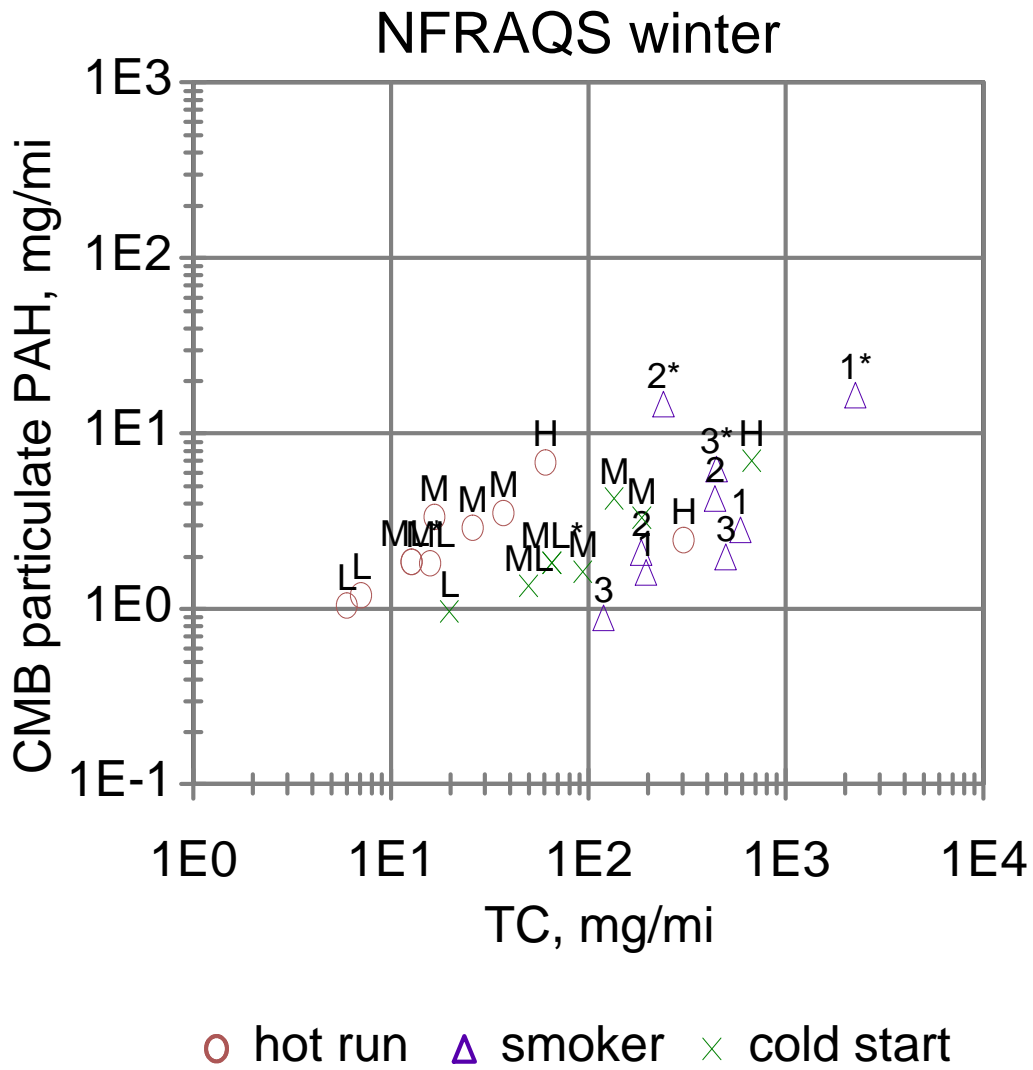


Figure 8. ‘Particulate’ PAH emissions measured in pooled exhaust samples from light-duty gasoline vehicles. The vertical coordinate shows the sum of the individual particulate PAHs included as fitting species in the final NFRAQS CMB. Format and data source are otherwise as in Figure 3.

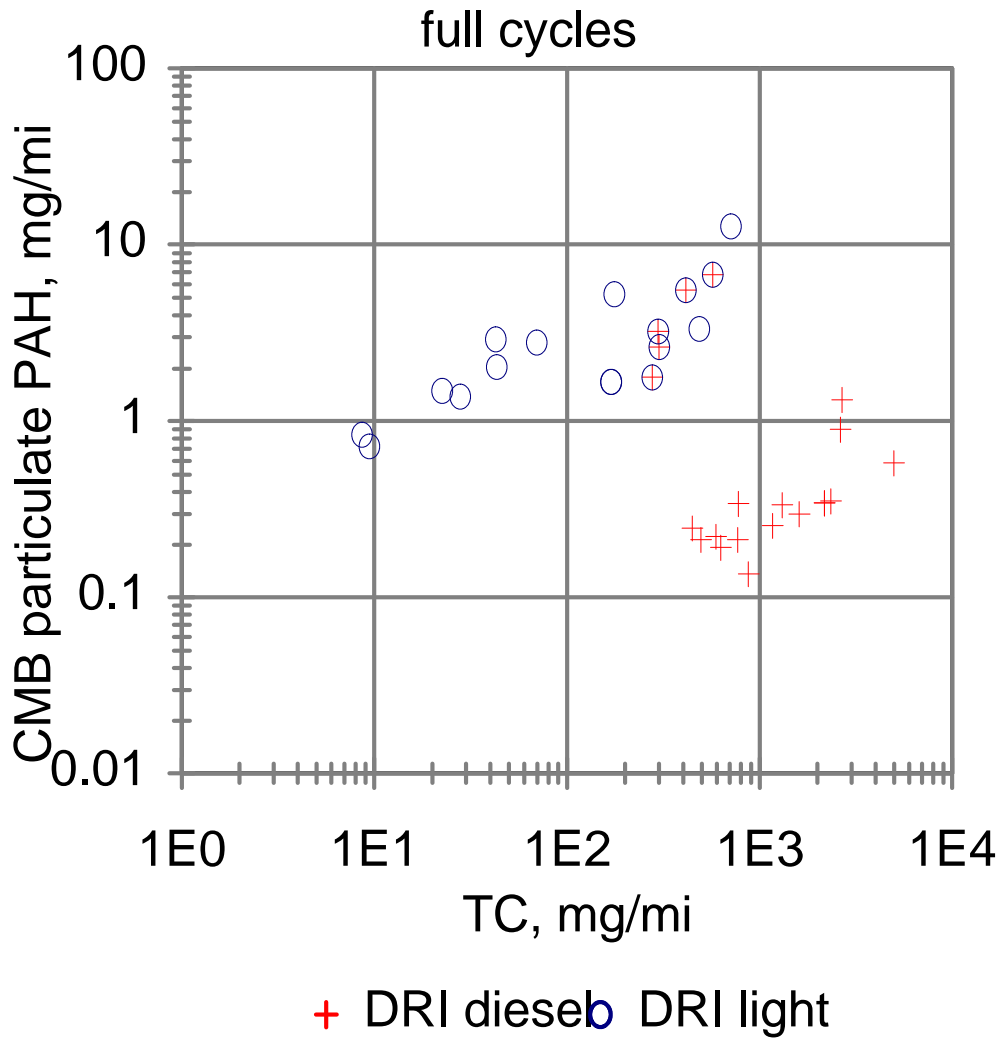


Figure 9. Full-cycle emissions of ‘particulate’ PAHs measured in tests of light- and heavy-duty gasoline and diesel vehicles. The vertical coordinate shows the sum of the individual particulate PAHs included as fitting species in the final NFRAQS CMB. Format and data source are otherwise as in Figure 4.

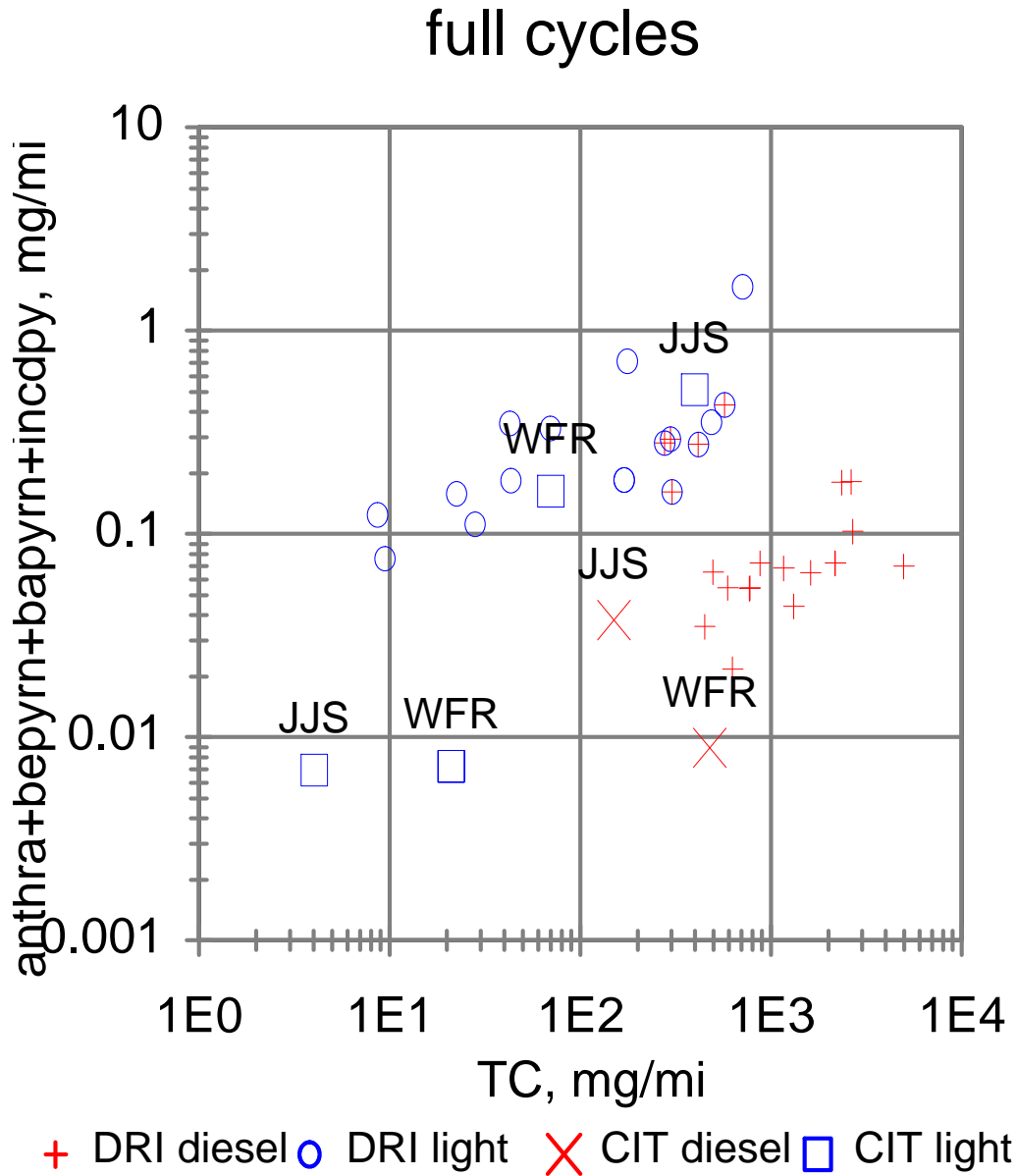


Figure 10. Full-cycle emissions of anthracene ('anthra'), benzo[e]pyrene ('bepyrn'), benzo[a]pyrene ('bapyrn'), and indeno[123-cd]pyrene ('incdpy') measured in tests of light- and heavy-duty gasoline and diesel vehicles. The plotted particulate PAHs were included in both the DRI and CIT measurements. Format and data sources are otherwise as in Figure 4.

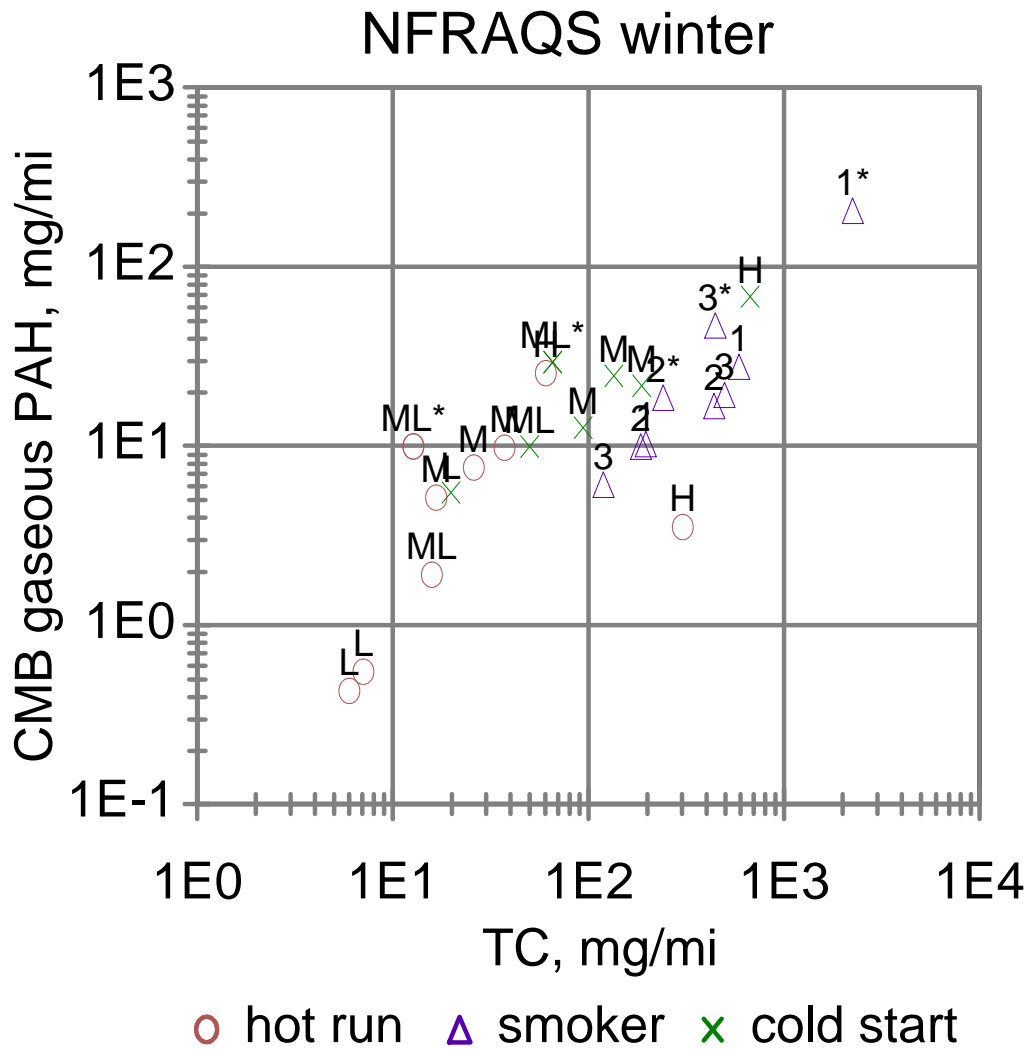


Figure 11. ‘Gaseous’ PAH emissions measured in pooled exhaust samples from light-duty gasoline vehicles. The vertical coordinate shows the sum of the individual gaseous PAHs included as fitting species in the final NFRAQS CMB. Format and data source are otherwise as in Figure 3.

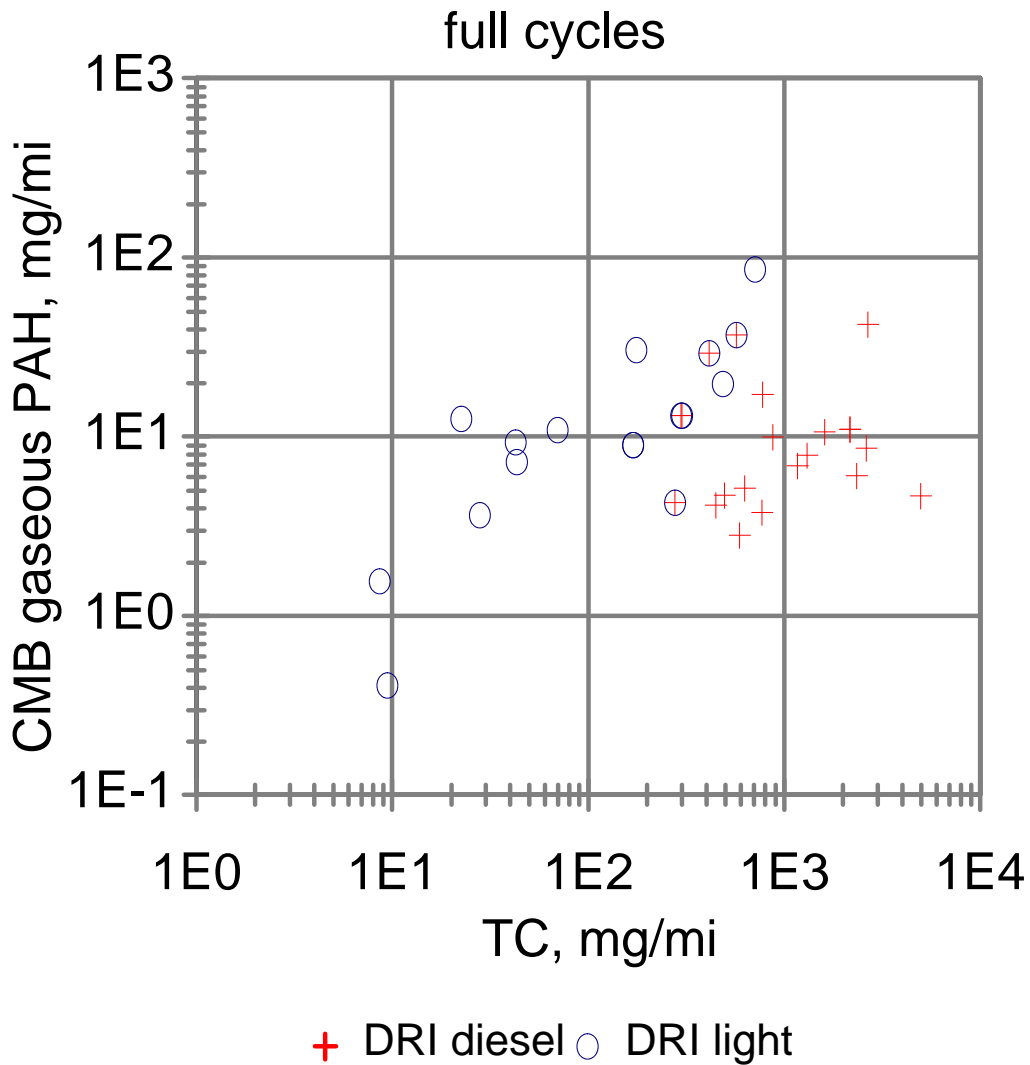


Figure 12. Full-cycle emissions of gaseous PAHs measured in tests of light- and heavy-duty gasoline and diesel vehicles. These compounds were not measured in the Rogge et al. (1993) and Schauer (1998) studies. The vertical coordinate shows the sum of the individual gaseous PAHs included as fitting species in the final NFRAQS CMB. Format and data sources are otherwise as in Figure 4.

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## Appendix C: Dimensions of variation in vehicle exhaust

Warren H. White, 9/24/00

This note extends the exploration of exhaust composition that *Homogeneity of vehicle exhaust* (7/27/00) began. The former note considered compounds one class at a time, plotting dynamometer-test data as mg/mi. The present note considers compound combinations representing the dimensions of observed chemical variation, and plots the same data as dimensionless mass ratios normalized to total carbon (TC).

The new format permits source-test data, CMB inputs, and CMB outputs to be overlain on the same plot, allowing the reader to visualize the connections among them. The cost of such multi-layering is a busy figure (e.g. Figure 1) that requires an investment from the reader. The return on this investment should be better feel for the relationships encoded in CMB analysis.

All data in this note are from the Northern Front Range Air Quality Study (NFRAQS) in Denver, supplied by Dr. Eric Fujita of DRI as electronic spreadsheets. It would be of interest to include data from a suite of more intensive chemical analyses of Los Angeles vehicle emissions (Rogge et al., 1993), but these are not available in electronic form. While Rogge et al. quantified some potentially useful marker species that could not be resolved in NFRAQS, they aggregated their exhaust samples into full-cycle composites for just 3 different vehicle groupings. NFRAQS, in contrast, distinguished exhaust samples from over 60 distinct vehicle groupings and operating modes, yielding a data set more suited to a study of composition variability. This note focuses on the results obtained over full FTP cycles for 15 light duty vehicle groups (10 gasoline and 5 diesel) and full warm-start truck cycles for 15 heavy-duty diesel vehicles.

DRI's analyses for NFRAQS reported over 100 distinct organic compounds. Some of these were detectable only in ambient air, some were detectable in vehicle exhaust but not in ambient air, and some were detectable in wood or charbroiler smoke but not in vehicle exhaust. The present analyses are limited to compounds usually quantifiable in vehicle exhaust. Listed in Table 1, these are elemental carbon (note that the organic fraction  $OC/TC = 1 - EC/TC$  is determined by the elemental fraction) and the 48 organic species whose signal/noise ratios (reported\_value/standard\_error) exceeded 4:1 in at least half of the vehicle exhaust groupings (15 of the 30 tests over complete cycles).

<u>short</u>	<u>long</u>	<u>short</u>	<u>long</u>
ectc	elemental carbon by TOR		
	<i>'gaseous' PAHs</i>		<i>'particulate' PAHs</i>
naphth	Naphthalene	phenan	Phenanthrene
mnaph2	2-menaphthalene	fluore	Fluorene
mnaph1	1-menaphthalene	a_mflu	A-Methylfluorene
dmn267	2,6+2,7-dimenaphthalene	m_1flu	1-Methylfluorene
dm1367	1,7+1,3+1,6-dimenaphthalene	b_mflu	B-Methylfluorene
d14523	2,3+1,4+1,5-dimenaphthalene	c_mflu	C-Methylfluorene
dmn12	1,2-dimenaphthalene	a_mpht	A-Methylphenanthrene
biphen	Biphenyl	m_2pht	2-Methylphenanthrene
m_2bph	2-Methylbiphenyl	c_mpht	C-Methylphenanthrene
m_3bph	3-Methylbiphenyl	m_1pht	1-Methylphenanthrene
m_4bph	4-Methylbiphenyl	dm36ph	3,6-Dimethylphenanthrene
atmnap	A-Trimethylnaphthalene	a_dmph	A-Dimethylphenanthrene
em_12n	1-Ethyl-2-methylnaphthalene	b_dmph	B-Dimethylphenanthrene
btmnap	B-Trimethylnaphthalene	c_dmph	C-Dimethylphenanthrene
ctmnap	C-Trimethylnaphthalene	dm17ph	1,7-Dimethylphenanthrene
etmnap	E-Trimethylnaphthalene	d_dmph	D-Dimethylphenanthrene
ftmnap	F-Trimethylnaphthalene	e_dmph	E-Dimethylphenanthrene
gtmnap	G-Trimethylnaphthalene	anthra	Anthracene
htmnap	H-Trimethylnaphthalene	m_9ant	9-Methylanthracene
acnapy	Acenaphthylene	fluora	Fluoranthene
acnape	Acenaphthene	pyrene	Pyrene
		c_mpyr	C-Methylpyrene
		<i>lactones, sterols, hopanes, steranes</i>	
		gnonla	G-Nonanoic Lactone
		ergostane	ergostane
		c27rch	cholestane-1 (C27 20R-5@,14B,17B-cholestane)
		ab30nh	norhopane-1 (17@(H),21B(H)-30 -Norhopane)
		ab_hop	hopane-1 (17@(H),21B(H)-Hopane)

Table 1. Organic compounds measured with better than 25% analytical precision over full FTP or truck cycles in at least half of the NFRAQS vehicle groupings. Compound identifiers and groupings are as employed in NFRAQS.

Figure 1 summarizes the abundance of EC and ‘particulate’ polycyclic aromatic hydrocarbons (PAHp) in various exhaust mixtures. EC has sometimes been employed as a surrogate metric for exposure to diesel exhaust (EPA, 2000), while PAHp consistently distinguished gasoline from diesel exhaust in the NFRAQS tests (*Homogeneity of vehicle exhaust*, Tables 8-10). (Schauer et al. (1996) supports the EC = diesel approximation, attributing about 95% of 1982 EC in downtown Los Angeles to diesel exhaust, but Watson et al. (1998) attributes much of the winter NFRAQS EC to non-diesel sources.)

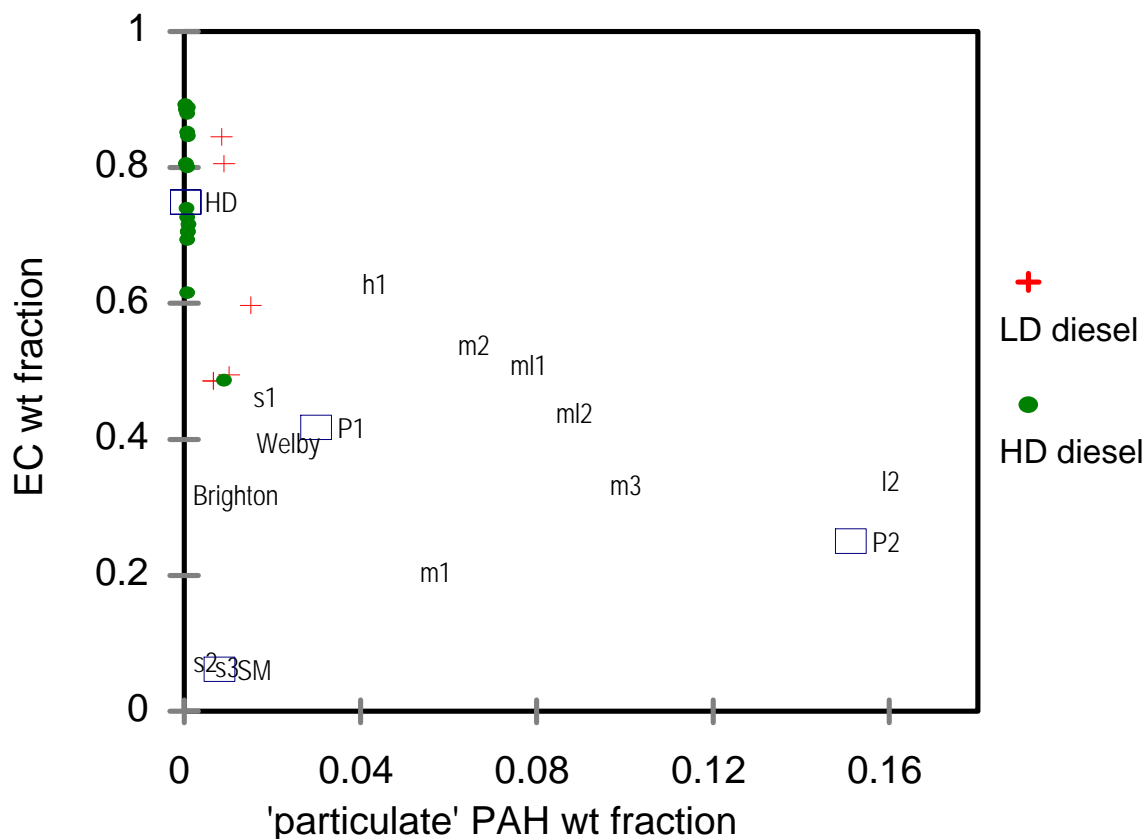


Figure 1. EC and PAH contents of exhaust from various vehicles and vehicle groupings sampled in NFRAQS. All contents are expressed as grams of compound per grams of total (elemental+organic) carbon. Data from individual light and heavy duty diesel vehicles operated on FTP and heavy truck cycles are indicated by symbols. Data from groups of light duty gasoline vehicles operated on the FTP cycle are indicated by the lower case identifiers: l2 (low emitters), ml1- ml2 (medium-low emitters), m1- m3 (medium emitters), h1 (high emitters), and s1- s3 (visibly smoking vehicles). (Groups l1 and h2 lack data for the cold-start portion of the FTP.) Squares with capitalized labels indicate the composite profiles used as inputs to the NFRAQS extended-species CMB: P1 and P2 (non-smoker), SM (smoker), and HD (heavy duty diesel). The non-smoker profiles represent different operating modes: P1 ('cold start'-- phase 1 of the FTP), and P2 ('hot stabilized'-- phase 2 of the FTP). Finally, the average winter mix of ambient vehicle exhaust estimated by the NFRAQS extended-species CMB is indicated by the centered labels 'Brighton' and 'Welby'.

Figure 1 depicts EC and PAH<sub>p</sub> contents for ambient mixtures (Brighton and Welby) as well as individual and composited source samples. The ambient data refer only to the contribution of vehicle exhaust, not to total ambient particulate matter, and are accordingly based on CMB estimates rather than direct measurement. The figure's graphical point is that, under the assumptions of the CMB, ambient compositions must be weighted vector averages of the contributing source compositions. With two chemical dimensions (EC and PAH<sub>p</sub>) in our plot, it is geometrically clear that we should be able to represent any ambient composition as a unique combination of three given source compositions. (The problem is analogous to placing three weights so as to balance a rigid and weightless plate on the tip of a vertical spindle. Physical reality of course requires that all source contributions be non-negative, so the ambient mix must lie within the triangle formed by the three sources.) With  $n$  chemical dimensions, we can correspondingly determine unique weightings for  $n+1$  different source compositions.

Figure 1a is a focused version of Figure 1, showing only the Brighton mixture and the four vehicle profiles used in the NFRAQS CMB. The Brighton composition is shown to lie near the line between the diesel (HD) and smoker (SM) profiles, meaning that it can be approximated as a linear combination of just these two sources. Brighton is slightly closer to the smokers than it is to the diesels, meaning that smokers will be the more heavily weighted in this combination. From simple inspection, therefore, we can conclude that Brighton vehicle exhaust is dominated by smokers and diesels, with smokers the more important of the two. The exact CMB estimate is in fact 56% smokers, 32% diesels, 9% cold starts (P1), and 3% hot-stabilized gasoline vehicles

(P2). (It should be recalled that this CMB estimate is what provided the EC and PAH<sub>p</sub> contents used to locate ambient exhaust composition in the plot. If CMB analysis had attributed more of the observed ambient OC to charbroiler and wood smoke, for example, that would have left ambient exhaust with a higher EC/(EC+OC) ratio. The higher EC content would have raised Brighton's position in the plot, moving it closer to the diesel profile.)

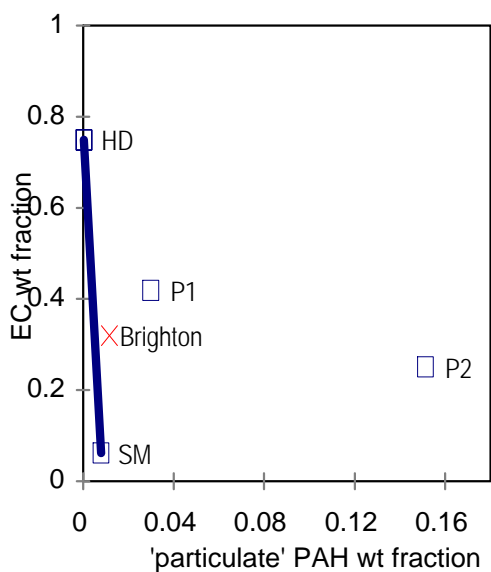


Figure 1a.

Figure 1b offers a similar focus on the Welby mixture. The essential difference between Welby and Brighton is that the Welby composition is much closer to that of the cold-start gasoline profile. The CMB accordingly weights cold starts much more heavily in the Welby mixture, which is estimated as 32% cold starts, 31% smokers, 30% diesels, and 8% hot-stabilized gasoline vehicles. (The reader should again note the apparent circularity of the preceding phrasing. In reality, Welby is plotted near the cold-start profile because the CMB estimates a significant cold-start contribution, not *vice versa*.)

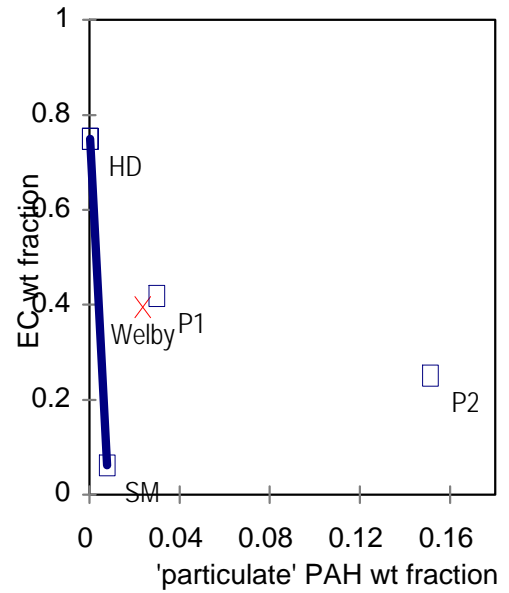
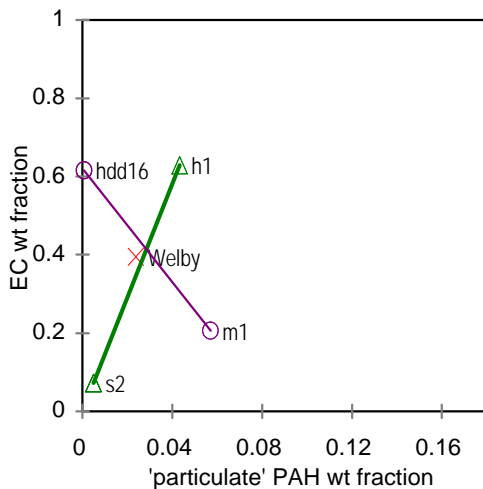


Figure 1b.

Having trained our eyes on Figures 1a and 1b, we can now return to the full Figure 1 with a new appreciation of its implications for E-59. The observed EC and PAHp contents of ambient exhaust in Brighton and Welby can be reproduced by many different combinations of vehicles, and different combinations yield different estimates for the gas/diesel split. Figure 1c shows, for example, how the EC and PAHp contents observed in Welby exhaust could arise from either a



wholly gasoline-fueled fleet (combining smokers and non-smoking high-emitters) or a 50-50 mix of gasoline and diesel vehicles. The ambiguity illustrated by Figure 1c in no way invalidates the CMB approach, but simply points to the need for independent information on fleet composition as an input.

Figure 1c.

Attention has so far been restricted to preselected exhaust constituents, EC and PAH<sub>p</sub>, and these might not be the most informative dimensions in the space of all chemical compositions. We obviously cannot visually assimilate all 49 dimensions (cf. Table 1) of this space, but we can use standard matrix decomposition techniques (Jolliffe, 1986) to identify the chemical dimensions that contribute the most variability in exhaust composition. It turns out that two dimensions, properly chosen, are sufficient to account for most of the total variance in the individual profiles. These dimensions, or principal components, are specified by linear combinations of the 49 resolved species as indicated in Figure 2. Figure 3 replots the data of Figure 1 in this alternative coordinate system.

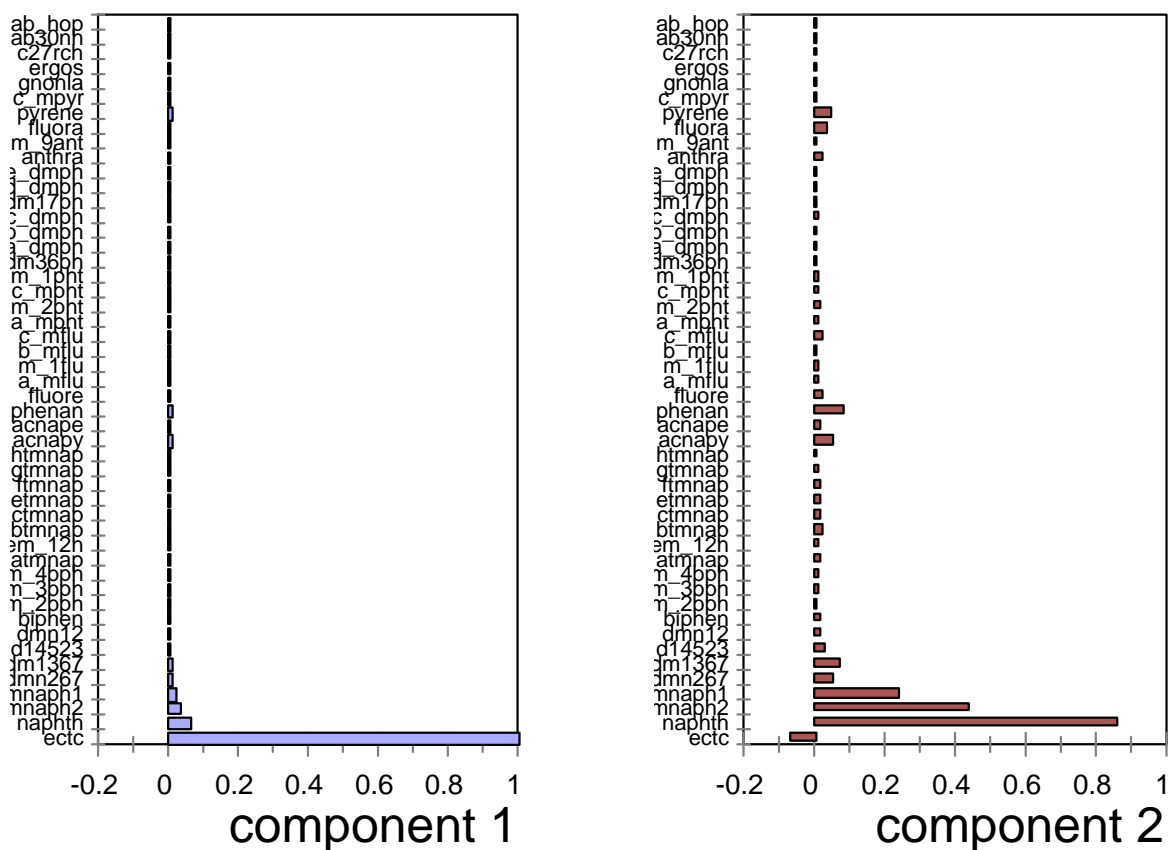
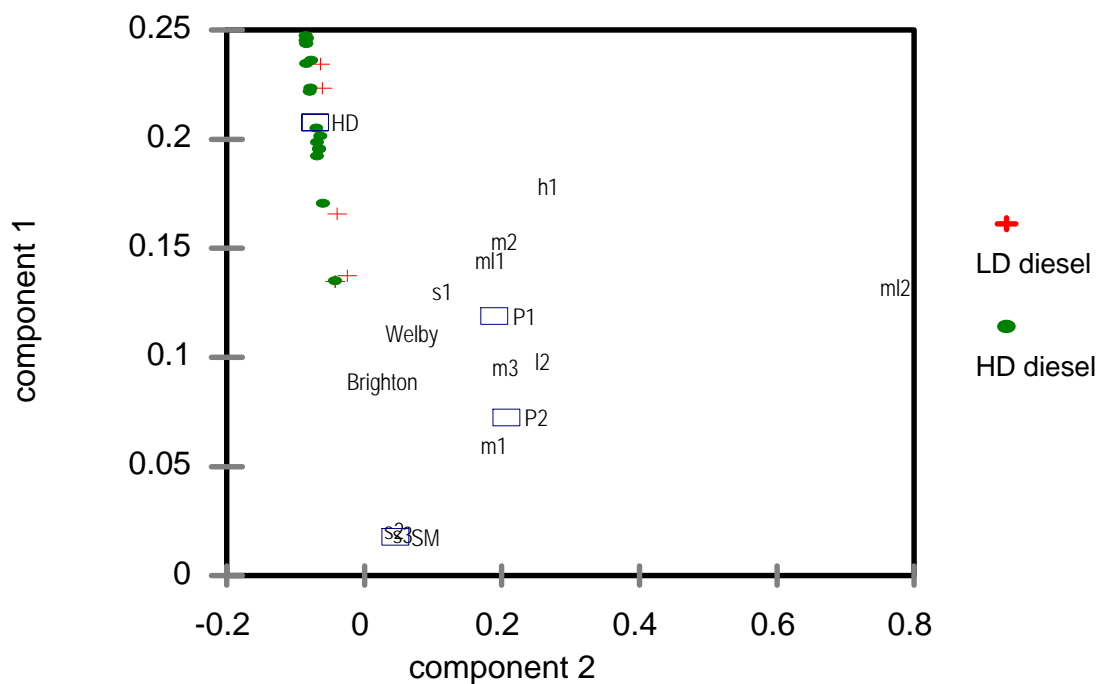


Figure 2. Normalized compositions for the plotting axes in Figure 3. Species are as in Table 1.



**Figure 3.** Data and format of Figure 1 projected into the chemical plane indicated in Figure 2.

The vertical axis of Figure 3 (component 1) is closely aligned with EC and the figure as a whole is rather similar to Figure 1, suggesting that the original coordinates EC and PAH<sub>p</sub> supplied much of the useful information on exhaust composition. The involvement of naphthalene and other ‘gaseous’ PAHs in the horizontal axis (component 2) eliminates the distinction ‘particulate’ PAHs drew in Figure 1 between some of the light- and heavy-duty diesels. The influence of ‘gaseous’ PAHs in Figure 3 also highlights the anomalous character of one of the ‘medium-low’ groups (ml2), which DRI for this reason excluded from its CMB profile for hot-stabilized emissions.

The plotting axes used in Figure 3 were chosen to account for inter-vehicle variance in the absolute fractions of TC contributed by individual species. This selection criterion preferentially weights constituents like EC and naphthalene that supply much of the total mass, regardless of whether they supply useful distinctions between vehicle classes. An alternative approach is first to re-scale each compound to exhibit unit variance across all 30 vehicle groupings, thereby placing them all on an equal footing. Applying the same matrix

decomposition techniques to the 48 trace compounds (omitting EC) re-scaled in this manner then yields new principal components, the first four of which serve as axes for the various projections in Figure 4.

Figure 4 shows the data of Figure 1 projected into chemical planes that maximize the relative variation in exhaust composition as described above. Some of the new axes offer enhanced resolution within seemingly homogeneous vehicle classes: for example, component 3 varies considerably over the class of diesels, and fairly well distinguishes light-duty from heavy-duty members of this class. None, however, offer clearly improved discrimination between the diesel and gasoline fleets.

The NFRAQS explorations sketched in this note can be summarized as follows:

**Variations in exhaust composition within vehicle classes are substantial relative to mean differences in exhaust composition between vehicle classes.**

This variability means that CMB-based source attributions are likely to be sensitive to the selection of vehicles for exhaust characterization. The resulting sampling error is beyond the corrective capacity of any theoretical analysis, and is likely to dominate the overall uncertainty of CMB estimates. It can be addressed only by improvements in experimental design: (a) increasing the number and representativeness of vehicles recruited for testing, and/or (b) measuring additional marker compounds that are more specific to particular vehicle categories.

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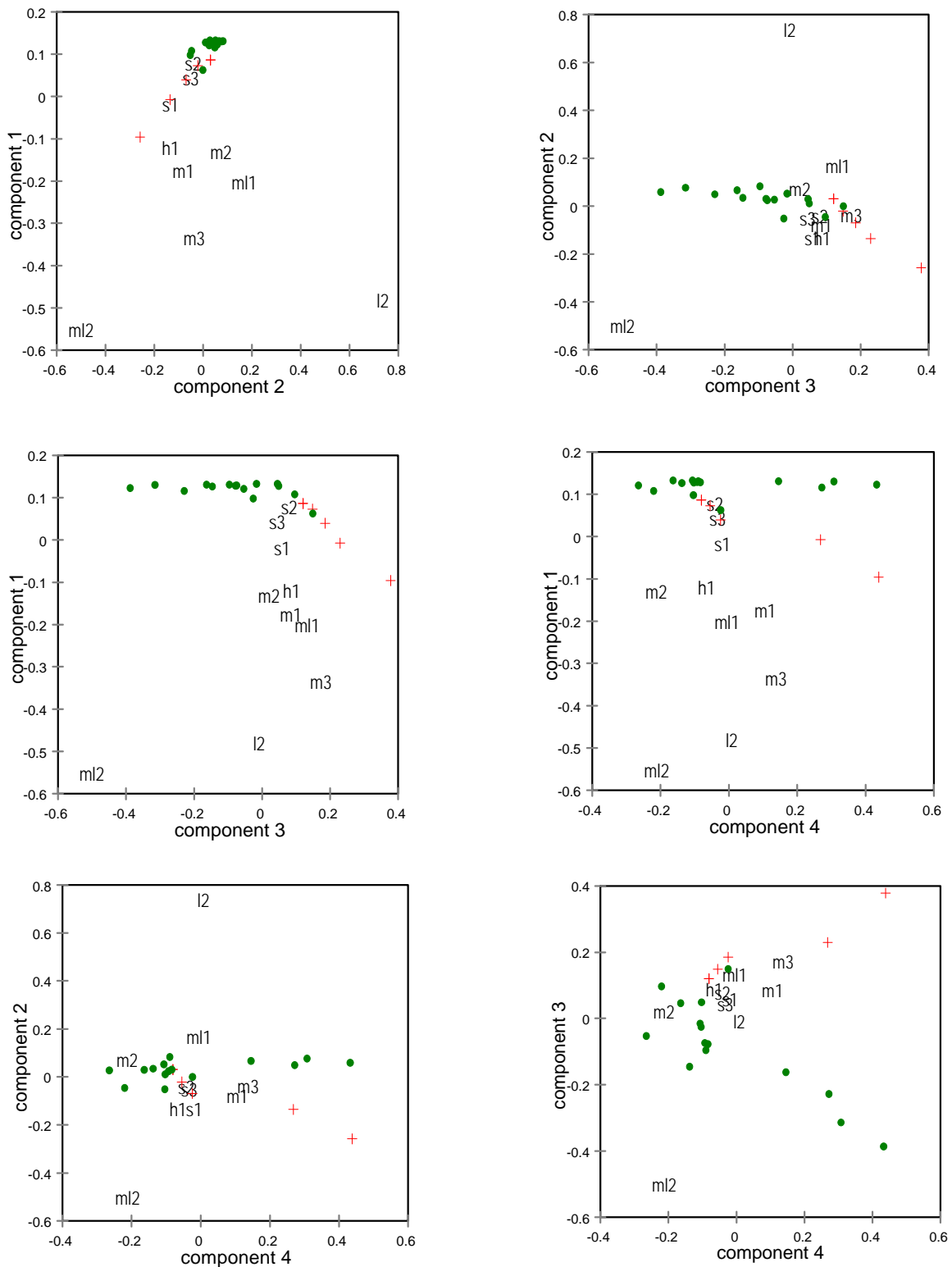
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**Figure 4.** Projections of exhaust composition on principal components of the re-scaled NFRAQS data matrix, as described in text. Plotting symbols are as in Figure 1.

## Appendix D: Types of uncertainty in CMB estimates

Warren H. White, 8/22/00

Let us discuss the uncertainty of CMB estimates in the simplest possible setting: this is the case in which we can identify a marker compound that serves as a unique tracer for exhaust from a specific category of vehicles and operating conditions. Let

$M$  = the fine PM (or OC) emitted by this source category, and let

$x_i$  = the chemical constituent of  $M$  with no other source of emissions (the 'tracer').

(The more general case, in which we have multiple marker compounds which are emitted in differing relative amounts from multiple sources, would get us into matrix rather than scalar notation. Otherwise, it is completely analogous.)

It will be helpful to have some consistent notation for the discussion to follow:

$[ ]$  = the true mass concentration in the ambient air volume of interest,

$[ ]_a$  = the measured mass concentration in our sample of ambient air,

$\langle \rangle$  = the true mass ratio in the aggregate exhaust from the vehicle population of interest,

$\langle \rangle_a$  = the true mass ratio in the aggregate exhaust from vehicles that contributed to our ambient sample,

$\langle \rangle_s$  = the measured mass ratio in the aggregate exhaust from the vehicle subpopulation and operating cycle selected for dynamometer testing.

The ambient concentration  $[x_i]_a$  is directly observable but  $[M]_a$  is not, because ambient  $M$  is indistinguishable from ambient PM or OC originating from other source categories. According to the above definitions, the true concentrations are related as follows:

$$[M] = [x_i] / \langle x_i / M \rangle_a. \quad [1]$$

We can measure  $[x_i]_a$  as an estimate of  $[x_i]$ , and can run dynamometer tests to obtain  $\langle x_i / M \rangle_s$  as an estimate of  $\langle x_i / M \rangle_a$ . Substituting these approximations into [1] yields our source attribution:

$$[M]_{\text{estimated}} = [x_i]_a / \langle x_i / M \rangle_s. \quad [2]$$

The uncertainty in this attribution can be estimated by examining the likely errors in numerator and denominator.

The error  $\varepsilon = [x_i]_a - [x_i]$  in the numerator of [2] represents the familiar type of uncertainty that arises from errors in sampling and analysis. It is usual, and reasonable, to assume that  $\varepsilon$  varies randomly from sample to sample if measurements are made with sufficient care. In this case we can average over sufficiently many independent ambient samples to make the relative error  $(\text{mean}[x_i]_a - \text{mean}[x_i]) / \text{mean}[x_i]$  as small as we wish.

The error in the denominator of [2] can be broken into two distinct components,  $\langle x_i/M \rangle_s - \langle x_i/M \rangle_a = (\langle x_i/M \rangle_s - \langle x_i/M \rangle) + (\langle x_i/M \rangle - \langle x_i/M \rangle_a)$ . The component  $\langle x_i/M \rangle - \langle x_i/M \rangle_a = \delta$  arises from spatial and temporal variations in the mix of the various vehicle categories and operating conditions. Some of  $\delta$  can be regarded as random like  $\epsilon$ , arising from such variables as traffic incidents and weather conditions. However, there may also be systematic dependences on location (e.g., urban core vs interstate highway) and time (e.g., Wednesday rush hour vs Sunday morning). Our ambient sampling program must balance these systematic influences if we hope to ‘average out’ their effects on our attribution.

The component  $\langle x_i/M \rangle_s - \langle x_i/M \rangle = \delta'$  arises from the failure of dynamometer tests on a sample of vehicles to reproduce the exact overall composition of real-world exhaust. Unlike  $\epsilon$  and  $\delta$ ,  $\delta'$  does not ‘average out’ with increased ambient sampling, and can be addressed only by added source testing. The scatter plots in my earlier note, *Homogeneity of vehicle exhaust*, suggested that values of  $\langle x_i/M \rangle_s$  determined for different samples from the same category of vehicles can vary by factors of 2 or 3. Source attributions based on these values would retain this same level of uncertainty, regardless of how many ambient samples they were averaged over.

The above considerations indicate that the number of dynamometer tests in E-59 will be driven by the need to develop composite dynamometer profiles  $\langle x_i/M \rangle_s$  that reliably simulate the mean profiles  $\langle x_i/M \rangle$  of real-world exhaust. Previous analyses have not fully accounted for the effects of the systematic profile errors introduced by  $\langle x_i/M \rangle_s - \langle x_i/M \rangle = \delta'$ . The NFRAQS analysis properly estimated the variance in  $\langle x_i/M \rangle_s - \langle x_i/M \rangle_a$ , including contributions from both analytical error and observed differences in exhaust composition. However, the propagated uncertainties in the apportionments for individual days were then treated statistically as being wholly independent of each other, neglecting the systematic influence of imperfectly representative source measurements. The uncertainties estimated for mean NFRAQS apportionments (e.g. Table 7.3-1 et. seq.) are therefore unrealistically low. The Caltech study did not include the multiple source tests needed to characterize variations in exhaust. That group’s propagation of uncertainty accordingly focused on the random component contributed by analytical error.

My discussion thus far can legitimately be faulted for its restriction to the case where a source is distinguished by a single tracer compound. In actual applications, numerous marker compounds may be available for the same source. Let us list these as  $x_1, x_2, \dots, x_k$ . (For simplicity, we will stay within the setting where all are ‘unique’ tracers, with no other sources.) In this case we can extend our source attribution equation [2] to an over-determined system of

equations:

$$\begin{aligned} [M]_{\text{estimated}} &= [x_1]_a / \langle x_1/M \rangle_s, \\ [M]_{\text{estimated}} &= [x_2]_a / \langle x_2/M \rangle_s, \\ &\dots \\ [M]_{\text{estimated}} &= [x_k]_a / \langle x_k/M \rangle_s. \end{aligned} \tag{3}$$

Least-squares techniques can be used to obtain a ‘solution’ to system [3] that minimizes the discrepancy between the observed ambient composition  $[x_1]_a, [x_2]_a, \dots, [x_k]_a$  and the dynamometer profile  $\langle x_1/M \rangle_s, \langle x_2/M \rangle_s, \dots, \langle x_k/M \rangle_s$ . The standard CMB software assumes the errors  $\langle x_i/M \rangle_s - \langle x_i/M \rangle_a$  for different species in our source profile to be statistically independent of one another, modeling them as noise from random measurement error. Their calculated effects on the solution accordingly tend to ‘average out’ as the number  $k$  of available tracers increases. The theoretical redundancy in system [3] thus seems to reduce our need for certainty in the source profile. This redundancy can be more apparent than real, however.

As noted earlier, uncertainties in the source profile arise from imperfectly representative vehicle sampling and test cycles in addition to the measurement errors associated with any chemical analysis. The scatter plots in *Homogeneity of vehicle exhaust* suggest that the effects of unrepresentative dynamometer testing can in fact dwarf the analytical errors for many species. Unfortunately, variations in exhaust composition can have highly correlated effects on the tracer abundances  $\langle x_i/M \rangle_s$ . Table 1 shows an example of inter-species correlations observed for the errors  $\langle x_i/M \rangle_s - \langle x_i/M \rangle_a$ , when NFRAQS dynamometer data from individual test groups are used to estimate the composite profile for hot-stabilized emissions. The benefits of using multiple tracers in this situation are largely illusory, as the additional compounds carry little in the way of new information.

	phenan	fluore	a_mflu	c_mflu	a_mpht	m_2pht	c_mpht	m_1pht	dm36ph	a_dmph	c_dmph	dm17ph	anthra	fluora	pyrene	a_mpyr	c_mpyr
phenan	1.00	0.88	0.88	0.77	0.91	0.88	0.88	0.87	0.76	0.74	0.77	0.76	0.86	0.82	0.87	0.59	0.67
fluore	0.88	1.00	0.68	0.79	0.63	0.61	0.58	0.59	0.52	0.49	0.50	0.50	0.66	0.65	0.65	0.38	0.50
a_mflu	0.88	0.68	1.00	0.67	0.86	0.77	0.81	0.75	0.58	0.54	0.59	0.57	0.72	0.60	0.70	0.32	0.39
c_mflu	0.77	0.79	0.67	1.00	0.65	0.63	0.58	0.61	0.57	0.55	0.53	0.53	0.58	0.64	0.66	0.32	0.55
a_mpht	0.91	0.63	0.86	0.65	1.00	0.98	0.97	0.98	0.90	0.89	0.91	0.90	0.92	0.88	0.92	0.65	0.78
m_2pht	0.88	0.61	0.77	0.63	0.98	1.00	0.98	1.00	0.96	0.94	0.96	0.94	0.96	0.94	0.94	0.75	0.86
c_mpht	0.88	0.58	0.81	0.58	0.97	0.98	1.00	0.98	0.90	0.87	0.92	0.90	0.95	0.89	0.90	0.76	0.76
m_1pht	0.87	0.59	0.75	0.61	0.98	1.00	0.98	1.00	0.96	0.95	0.97	0.95	0.95	0.93	0.93	0.77	0.86
dm36ph	0.76	0.52	0.58	0.57	0.90	0.96	0.90	0.96	1.00	0.99	0.99	0.99	0.89	0.98	0.96	0.83	0.96
a_dmph	0.74	0.49	0.54	0.55	0.89	0.94	0.87	0.95	0.99	1.00	0.99	0.98	0.87	0.95	0.93	0.80	0.97
c_dmph	0.77	0.50	0.59	0.53	0.91	0.96	0.92	0.97	0.99	0.99	1.00	1.00	0.89	0.96	0.95	0.85	0.95
dm17ph	0.76	0.50	0.57	0.53	0.90	0.94	0.90	0.95	0.99	0.98	1.00	1.00	0.86	0.97	0.96	0.87	0.95
anthra	0.86	0.66	0.72	0.58	0.92	0.96	0.95	0.95	0.89	0.87	0.89	0.86	1.00	0.89	0.85	0.74	0.79
fluora	0.82	0.65	0.60	0.64	0.88	0.94	0.89	0.93	0.98	0.95	0.96	0.97	0.89	1.00	0.98	0.85	0.95
pyrene	0.87	0.65	0.70	0.66	0.92	0.94	0.90	0.93	0.96	0.93	0.95	0.96	0.85	0.98	1.00	0.81	0.90
a_mpyr	0.59	0.38	0.32	0.32	0.65	0.75	0.76	0.77	0.83	0.80	0.85	0.87	0.74	0.85	0.81	1.00	0.81
c_mpyr	0.67	0.50	0.39	0.55	0.78	0.86	0.76	0.86	0.96	0.97	0.95	0.95	0.79	0.95	0.90	0.81	1.00

Table 1. Correlations among compounds in LDGV exhaust. Values give product-moment correlation coefficients ( $r$ ) for the mass fractions  $\langle \text{species\_mass\_}(\text{mg}/\text{mi})/\text{total\_mass\_}(\text{mg}/\text{mi}) \rangle$ . Data are from NFRAQS measurements of exhaust from eight groups of non-smoking LDGVs in hot-stabilized operation (normalized profiles L1P2, L2P2, ML1P2, M1P2, M2P2, M3P2, H1P2, H2P2). The listed compounds, identified as in the NFRAQS report, are all particulate PAH's that were measured with precisions of 10% or better. Correlations throughout the highlighted region exceed 85%. The critical value for one-sided statistical significance at the 1% level is  $r = 0.79$ .

## Appendix E: Measurement of EC

Warren H. White, 10/31/00

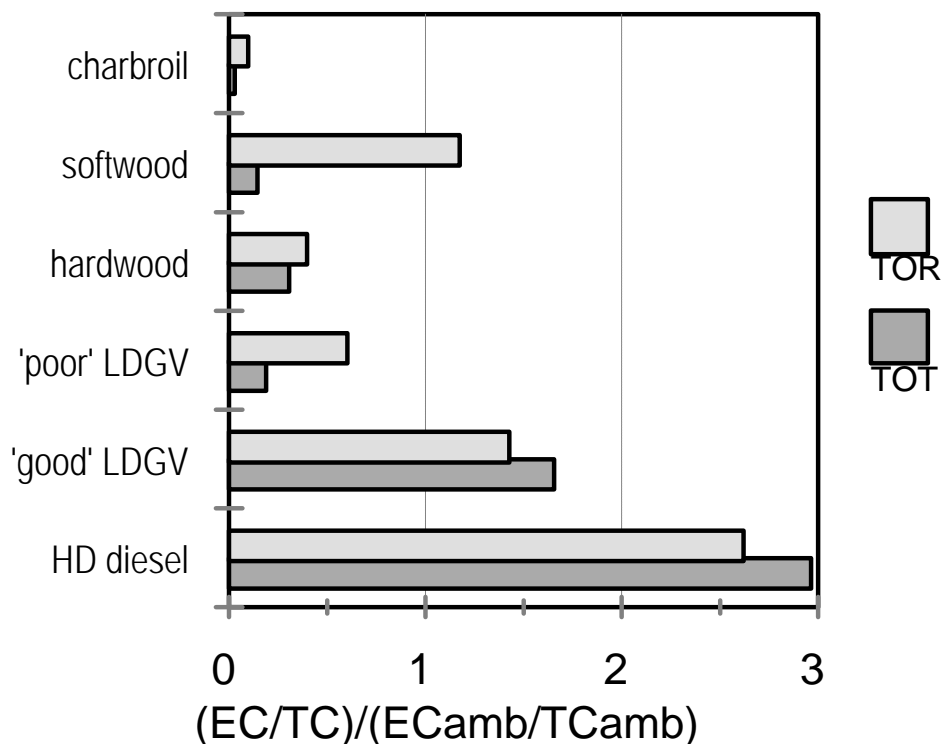
Two different thermal-optical procedures are widely used to determine the fraction of a sample's total carbon present in the reduced, or "elemental," form. These are variously identified as the TOT/Sunset Labs/NIOSH and TOR/DRI/IMPROVE methods, and they are known to yield substantially different EC/OC splits (Countess, 1990; Chow et al., 2000; Norris et al., 2000). Both methods evolved from a common ancestor (Johnson et al., 1981) over the course of a decade or more, complicating the interpretation of trends and the integration of data from different studies, particularly those from different years. This situation will likely continue, as the nation has invested in two large ambient monitoring networks (IMPROVE and PM<sub>2.5</sub> speciation), the former employing the IMPROVE method and the latter the NIOSH method.

In NFRAQS, DRI used the TOR method employed in the IMPROVE network. In its study of Los Angeles, the Caltech group used the TOT method employed in the PM<sub>2.5</sub> speciation network. Table 1 compares results from the two studies.

	DRI (Denver)	Caltech (Los Angeles)
heavy-duty diesel	80%	55%
LDGV, good cond'n	43%	31%
LDGV, poor cond'n	18%	3%
meat charbroiling	2%	0%
softwood, fireplace	35%	2%
hardwood, fireplace	11%	5%

Table 1. "Elemental"/total carbon ratios (EC/TC) measured in two different emissions characterization studies. Values under the DRI heading were determined by the thermal-optical reflectance (TOR) method and are from the following NFRAQS composite source profiles (Watson et al., 1998; Fujita, 2000): heavy duty diesel vehicles, truck cycle (NWHD); non-smoking light duty gasoline vehicles, FTP (NWN<sub>SPC</sub>); visibly smoking light duty gasoline vehicles, FTP (NW<sub>SCPC</sub>); meat charbroiler (NMc); fireplace burning soft woods (NWF<sub>Sc</sub>); fireplace burning hard woods (NWF<sub>Hc</sub>). Non-diesel values under the Caltech heading are from Schauer (1998), with the condition of LDGVs referring to the presence ('good') or absence ('poor') of an exhaust catalyst. They are more recent than those used in the Schauer et al. (1996) apportionment, and were determined by the current thermal optical transmittance (TOT) method. The Caltech heavy-duty diesel value is from Rogge et al. (1993), and was determined by an earlier implementation of the TOT method.

Measurements of ambient EC by TOR and TOT typically track each other well. The U.S. EPA recently made collocated measurements in Philadelphia and Phoenix (twenty 24h samples at each location), and found TOR EC to be about twice TOT EC with correlation coefficients exceeding 95% (Norris et al., 2000). The disagreement is not a matter simply of calibration, however, as the two methods respond differently to individual components of the ambient mix. As Figure 1 shows, diesels and low-emitting gasoline vehicles are the only source categories with emissions that are richer in TOT EC than typical ambient air is, while gasoline high-emitters and softwood burning strongly depress the ambient EC/TC fraction as measured by TOT. Most TOT EC in ambient air must therefore have come from diesel exhaust (assuming emissions from low-emitting gasoline vehicles to be relatively unimportant). Diesels and gasoline low-emitters are also rich in TOR EC, but so is softwood smoke, and even gasoline high-emitters only mildly depress the ambient EC/TC fraction as measured by TOR. In contrast to TOT EC, then, much of the ambient TOR EC could have come from softwood smoke and gasoline high-emitters.



**Figure 1.** Emitted EC/TC fractions from Table 1, normalized to ambient averages determined by collocated TOR and TOT measurements in Phoenix. (Recall that the source data were from measurements in Denver and Los Angeles.) Ambient samples were collected on 20 days during January-February 1999 (Norris et al., 2000); ambient values  $EC_{amb}/TC_{amb}$  were 31% (TOR) and 19% (TOT). TOR emissions data (DRI) are normalized to the TOR ambient value, and TOT emissions data (Caltech) are normalized to the TOT ambient value.

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## **Appendix F: Statistical Fleet-Sizing**

Richard F. Gunst, 10/24/00

The ultimate goal of statistical fleet sizing assessment is to ensure that a sufficient number of vehicles are included in a study so that the objectives of the study can, with a high degree of certainty, be achieved. This very straightforward goal is actually very complex due to a number of critical components of the fleet-sizing assessment process. In its simplest form, fleet-sizing first seeks to eliminate, to the greatest extent possible, potential biases due to nonrepresentativeness of the vehicles included in the test fleet. Second, subject to the elimination of potential biases, fleet-sizing seeks to reduce uncertainty in the statistical analysis of the study results. While attention is often focused on the second of these two fleet-sizing criteria, it is the first component that is more critical. Without a representative test fleet, a study with a massive number of vehicles can be as biased as a study with a small number of vehicles. It is in the context of these two fleet-sizing criteria that the following considerations are offered for the planning of the Los Angeles Gasoline-Diesel Apportionment Study.

### ***Definition of a Target Fleet***

Any study that simply measures emissions on a collection of vehicles neither ensures representativeness nor implicitly defines an appropriate fleet. Failure to have a representative sample of vehicles from a well-defined target fleet jeopardizes any potential conclusions from the study because an overabundance of some vehicle technologies and characteristics and a lack of others.

A fleet of target vehicles must be defined prior to the selection of vehicles. One of the major differences in the previous California and Denver apportionment studies is in the fleets that were recruited for the respective studies. While neither study may have intended their fleets to be representative of specific fleets, comparisons are being made of the studies' conclusions. Such comparisons can only be considered reasonable if the analyses are based on data from similar fleets (and other similarities, see below). Each study's conclusions can be considered biased toward the de-facto fleet represented by the recruited vehicles. There is no statistical method that can eliminate biases due to a nonrepresentative fleet. On the other hand, even a small study fleet that is representative of a predetermined target fleet will not suffer from biases due to overrepresentation or exclusion of classes of vehicles.

It must be stressed that a target fleet should be defined realistically within the constraints that are inherent in any major study of this type. Taken to extreme, fleet definition can be so detailed that no single study with reasonable budget, time, and personnel constraints could recruit a sufficiently representative number and diversity of vehicles. A study of the type envisioned for the Los Angeles Gasoline-Diesel Apportionment Study must compromise some detail for a general assessment of a California fleet. General categories of cars and trucks, with perhaps a few breakdowns by technology group, weight, etc. must suffice for the objectives of the study. The critical feature of this determination is that the fleet definition must be stipulated prior to fleet recruitment. It is understood that fleet recruitment for a pre-specified target fleet poses many difficulties. Nevertheless, failure to recruit a representative fleet from a pre-specified target fleet risks biases of an unknown nature that cannot be eliminated by a statistical analysis of the resulting data.

### ***Chemical Mass Balance Analysis***

A statistical chemical mass balance analysis, like all statistical analyses, draws its validity in part from the data used in the analysis. As with the previous discussion of fleet definition and recruitment, there are bias and uncertainty considerations in any assessment of apportionment resulting from a chemical mass balance analysis. As before, bias must be the first consideration.

The carbon sources used in a chemical mass balance analysis must encompass all major carbon sources in the Los Angeles basin. The California and Denver studies did not use the same sources. If either study failed to include an important carbon source that the other did include, the carbon effects of the excluded source(s) might be attributed to one or more of the included sources. This is another form of bias, similar to the exclusion of an important component of a targeted vehicle fleet. Moreover, if two carbon sources in a region produce similar species profiles, the chemical mass balance analysis requires that one be eliminated from the analysis. The remaining source then contains the combined effect of the two sources and one cannot unambiguously attribute the apportionment to the source that is retained.

The selection of sources is highlighted in this discussion of fleet sizing because it impacts apportionment just as bias due to a nonrepresentative fleet does. In addition, there may be tradeoffs between fleet recruitment and source selection in order for this project to remain within budget or within other project constraints. No less a consideration is the selection of ambient sites. For the same reason, if regional conclusions are to be drawn, a representative selection of sites must be included. A large number of sites is not needed,

but they must be representative of the region for which an apportionment is desired. Similar comments obviously hold for the chemical species that are to be measured at each source and at the ambient locations.

### ***Technical Requirements for Fleet Sizing***

Once a target fleet, sources, chemical species, and ambient locations have been identified, a technical assessment of the number of vehicles could proceed. There is, however, no simple formula that would provide a fleet size. Statistical sample size determination is based on tentative, “best-guess,” or “worst-case” information on the magnitude of effects expected and on the variability of measurements. In a simple case, the comparison of two means, one would need to specify the magnitude of the difference in the means that one would like to be able to detect and magnitudes of the variability (standard deviations) of the two sets of measurements. The variability estimates are usually determined from previous studies of the same type or on best-guess or worst-case specifications.

For the forthcoming Los Angeles gasoline-diesel apportionment study, estimates of mean emissions and of variability, or some specification of likely values, would need to be available for each of the vehicle classes that are part of the target fleet. Variability estimates or likely values would be needed for each of the chemical species, both at the ambient sites and at the sources. Also needed are estimates or likely values of the mean ambient species measurements and the mean species profiles for each of the sources. Another requirement for determining a fleet size would be a stipulation of how ambient and source measurements are to be combined to get composite measurements for use in the chemical mass balance equations.

With this information, one could perform simulations with randomly generated errors and assess the differences in source contributions that could be detected with a high degree of certainty. These simulations would be conducted with varying fleet sizes in order to make this assessment. Although such simulations can be performed, there is a very heavy burden on accurate apriori information for an assessment of fleet sizes.

### ***Final Considerations***

As detailed above, fleet sizing in a project of this scope is a complex process, one that relies on accurate information about all the measurements that are to be made. Often, this type of accurate information is not available, especially since targeted fleets usually

include classes of vehicles with newer technologies than vehicles for which emissions data are available. As a practical matter, in many studies actual fleet sizes are dictated by budget and operational constraints. Then the fleet sizing issue translates to one of allocation: how many vehicles to allocate to the different vehicle classes. The simpler allocation assignment follows a straightforward strategy: assign more vehicles to classes where greater emissions variability is expected. There should be no fewer than 2, preferably 3, vehicles in any vehicle class. More should be placed in high emitter and high emissions variability vehicle classes.