# CHAPTER 7

# TOP-DOWN ASSESSMENTS OF EMISSION INVENTORIES

This chapter uses some of the tools of Chapter 6 to estimate quantitative confidence limits on the emission estimates for a few of the more important source categories. This chapter illustrates through several examples the likely magnitude of uncertainty in aggregated national emissions and some specific urban or point sources. Only the U.S. NEI is directly considered here for three reasons. First, Canada and Mexico often follow U.S. inventory development techniques, so the uncertainty assessment techniques for the U.S. NEI will likely be applicable to those inventories as well. Second, the NEI is the U.S. inventory of greatest interest and applicability, and it is readily available for investigation through publicly accessible documents. Third, the states have reviewed and provided input for the U.S. NEI inventories for their areas as used for SIPs.

This chapter has two major objectives: first, to introduce various top-down techniques for evaluating the strengths and weaknesses of current inventories, and second, to provide evaluations, as far as possible, of important sectors of current inventories. Top-down tests of emission inventories are tests conducted outside the structure of the emission inventory. They do not explicitly consider the individual components (e.g., emission factors or activity factors) that go into the development of inventories from the bottom up. Rather they consider independent information such as ambient measurements of the emitted species. Thus, a top-down approach can be thought of as an attempt to partially confirm an inventory. Ideally, such a test is designed to address a critical aspect of an inventory in a simple and unambiguous manner.

Although top-down tests provide an indication of the accuracy of existing inventories, they do not provide clear guidance regarding the specific cause of any identified inaccuracies. Chapter 8 deals with

systematic approaches for quantifying inventory uncertainty from the bottom up; i.e., working within the structure of the inventory to derive a quantitative measure of the inventory uncertainty through uncertainty analysis and sensitivity analysis. These approaches are complementary to the top-down tests, because they can apportion the uncertainty to the various components that go into the inventory. Such apportionment is critical for identifying the most effective approach for improving inventories.

In the following, it is assumed that the ambient measurements or other independent information used in the evaluations are accurate, and that they are correctly interpreted for both national and local conditions. Any discrepancies identified are assumed to be due to weaknesses in the inventories, and, where possible, suggestions for the modification of the inventories are made so as to resolve the discrepancies. However, the accuracy and interpretation of the measurements may have weaknesses themselves. As reflected in Figure 2.1 and the discussion in Box 7.1, the discussion presented here must be considered as only the first step in a repetitive process of improving

**Box 7.1  Verification, Validation and Confirmation**

Oreskes et al. (1994) provide a useful context for assessing any emission inventory. They note that:

- In a rigorously defined sense it is impossible to verify or validate any numerical model. Such terms imply that the model is an exact representation of a real system, while any model is necessarily an incomplete description of reality.

- At best a model can be partially confirmed by demonstration of agreement between the results of the model and observational data. This confirmation increases confidence in the utility of the model for its designed purposes. However, the confirmation must remain incomplete because, regardless of how many confirmatory tests are satisfactorily completed, additional tests may reveal inconsistencies between the model and present or future observations.

both the inventories and their evaluation through these top-down tests. The ultimate goal is to bring the inventories and their evaluations into agreement.

# 7.1  EVALUATION OF ONROAD VEHICLE EMISSIONS IN THE UNITED STATES

Onroad vehicle emissions are perhaps the most important sector of the inventory relating to criteria or criteria-related pollutants because (1) they account for a major share of VOC, $NO_x$ and CO emissions; (2) these VOC emissions provide the majority of the most photochemically reactive VOCs; and (3) these emissions are localized in urban areas, which account for the majority of the NAAQS ozone violations. Accurate emission estimation for this source is difficult since it must entail the integration of the emission factors (e.g., grams / mile driven) for

a diverse, constantly evolving vehicle fleet multiplied by highly variable activity factors (e.g., average miles driven per unit time for each vehicle type under varying vehicle operating conditions such as ratios of cold starts or high-load accelerations). This section examines the reported onroad vehicle emissions of VOC, $NO_x$ and CO for internal consistency over the past two decades and identifies inconsistencies with ambient measurements, which may indicate weaknesses of the inventories. NRC (2000) notes that quantitative estimates of overall accuracy and uncertainty have not been provided for inventoried onroad emissions, due to the lack of available data. At least an initial assessment of the accuracy of these emission estimates is provided here.

Two features of this section should be noted. First, wherever possible, national emissions are tested, even though local, county-level emission inventories exist. This approach requires nationally representative data, rather than purely local measurements to reach as general conclusions as possible. However, studies of local or regional inventories can yield important tests of inventories; for example the investigation of the weekday-weekend effect in California have shed light on disparities in the MOBILE6 model (see e.g., Fujita et al., 2003a,b and other papers in that journal issue). Second, no evaluation of PM emissions from onroad vehicles has been included in this chapter; however developing better PM inventories is of high priority. Source apportionment studies have given an idea of how PM sources are divided between direct emissions and secondary formation in the atmosphere, and how the direct emissions compare with the emission inventories. Presently the MOBILE6.2 model does not cover high-emitting PM vehicles for either gasoline or diesel fuel classes; current work is underway to incorporate these high-emitters into the model.

## 7.1.1  History of Temporal Trends of Onroad Vehicle Emissions

The U.S. EPA regularly reports estimated emissions and their trends over the previous decades, generally in annual National Air Quality and Emissions Trends Reports. Recently these reports have been supplemented with emission tables posted on the website of the Technology Transfer Network:

Clearinghouse for Inventories & Emission Factors (http://www.epa.gov/ttn/chief/trends/index.html). This section compares a recent historical sample of these Trends Reports (U.S. EPA, 1990; 1995; 2000; 2003) with an earlier inventory developed for NAPAP (Saeger et. al., 1989) and the most recent emission tables (1970 – 2002; average annual emissions, all criteria pollutants - posted November 22, 2004 on the above website.) This comparison aims to determine if the estimated trends are converging to more precisely defined values, or if there is a significant element of scatter in the estimates that may indicate fundamental uncertainties in the estimation methods.

Figure 7.1 presents estimated onroad emissions from the six references listed above for VOC, $NO_x$ and CO. It is important to note that the 2004 Trends Tables utilize the latest MOBILE6 model, and that those tables are consistent with Version 3 of the 1999 U.S. NEI. All of the other reports use earlier versions of the model to estimate onroad vehicle emissions. In the following tests, greater emphasis will be placed on the two more recent reports for present and past years. The Trends Reports are revised from year to year; both the current year and prior year inventories are updated using the latest models and other information.

From the figure it is clear that the different inventory development techniques that have been used over the years have yielded results that differ in some important respects. For 1998 (the last year reported in the 2000 Trends Report) only minor increases of 10 and 14 percent are noted in the VOC and $NO_x$ emissions, respectively, between 2000 and the later estimates. However, the estimate for CO increased by 45 percent. These comparisons show that the most recent nationally aggregated emission estimates are different by at least ~10-15 percent for VOC and $NO_x$ and ~50 percent for CO. These comparisons suggest that there is significant uncertainty in the emission estimates.

Also of concern is the larger variability apparent in the estimates for earlier years. For example, for 1985 (the one year with estimates from all six inventories) the 2004 estimate is higher than all previous estimates by factors of up to 1.6, 1.4 and 2.5 for VOC, $NO_x$, and CO, respectively. These relatively large factors indicate that the onroad emission estimates for the
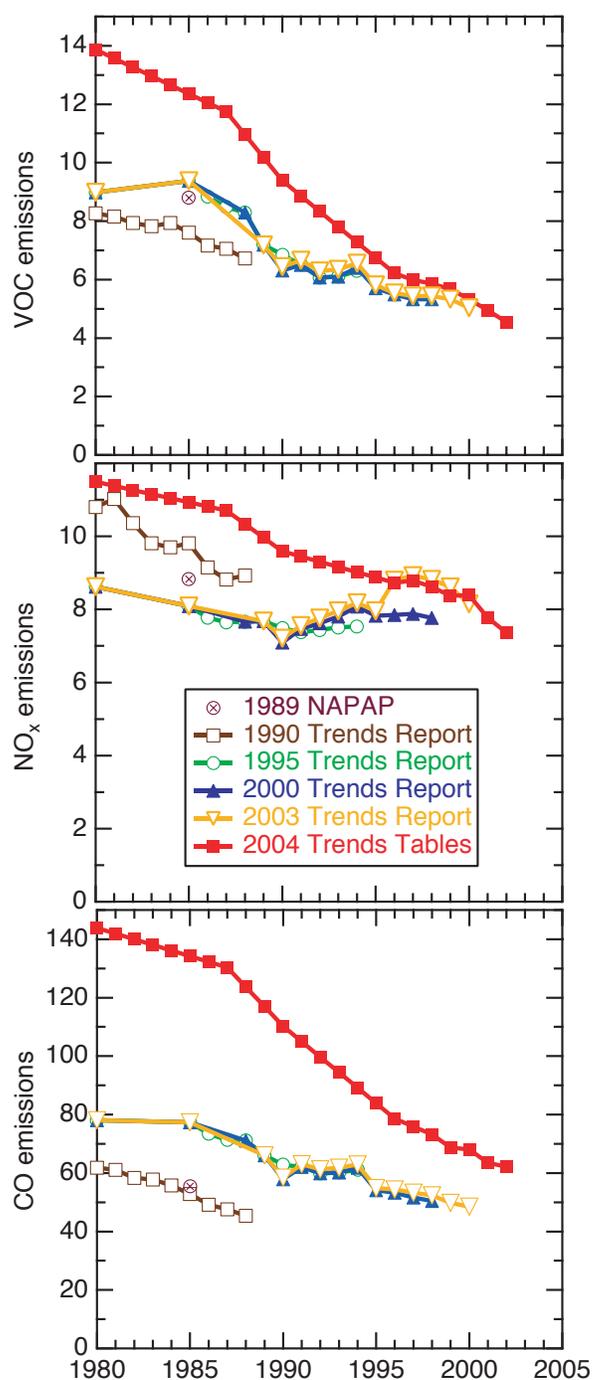


**Figure 7.1. National onroad vehicle emission estimates from six U.S. inventories in units of $10^6$ tons/yr.** All estimates are for onroad vehicle emissions only, except for NAPAP and the 1990 Trends Report which include total transport sources. For CO, NAPAP includes total area sources; these are the most detailed breakdowns available in the published reports. The dates indicate the year of publication of the inventory report.

past two decades are significantly less certain than the estimates for more recent years.

## 7.1.2 Temporal Trends of Onroad Vehicle CO Emissions Compared to Ambient Observations

Analysis of ambient measurements of emitted species can, in many instances, provide valuable insights into the magnitudes and temporal trends of the emissions that produce those ambient concentrations. The goal here is to use the temporal trend of ambient CO concentrations in U.S. urban areas to test the temporal trends of reported CO emissions from onroad vehicles. CO is selected for this analysis because reliable ambient measurements have been made over the last three decades at hundreds of urban stations throughout the U.S.

It is possible to select aggregated ambient CO data that closely reflect onroad vehicle emissions. The maximum CO levels observed in urban areas are utilized here. In 2002 (the latest year covered by the 2004 Trends Tables) 56 percent of total CO emissions are attributed to onroad vehicles, which are highly localized in urban areas. The maximum CO levels occur in winter, when urban emissions from the two other major CO sources are minimized. These sources are 22 percent from offroad vehicles, primarily lawn and garden and recreational vehicles, which maximize in the summer, and 15 percent from forest and agricultural burning, which also maximize in the summer and generally occur outside urban areas. A minor confounding factor is the background levels of CO likely transported into urban areas. However, these levels are a few tenths of a ppmv, so their influence can be neglected. Hence temporal trends in maximum urban CO levels can be confidently attributed to trends in CO emissions from onroad vehicles.

Figure 7.2 compares measured mean CO ambient levels with the emissions from Figure 7.1 for the two most recent emission reports. The ambient mixing ratios correspond to the mean maximum levels observed at more than 300 U.S. urban sites, which are tabulated in the U.S. EPA Trends Reports. (The statistic reported is the second highest annual maximum 8-hour average).

The trend of the mean ambient concentration follows the trend in the 2004 Trends Tables much more closely than that in the 2003 Trends Report. This suggests that the MOBILE6 model is correctly predicting the relative changes in CO emission rates with time. This conclusion is supported by the average 1985-2000 yearly decreases: 4.9 percent/year for the ambient concentrations compared to 4.9 and 2.8 percent/year for the 2004 Trends Tables and 2003 Trends Reports, respectively. However, while these comparisons indicate that the temporal trend in the 2004 Tables is more realistic than that in the 2003 Report, the comparisons provide no information regarding the accuracy of the emission magnitudes in any particular year or report.

## 7.1.3 Onroad Vehicle CO/NO$_x$ Emission Ratios Compared to Ambient Measurements

In favorable situations, ratios of ambient concentrations can be directly compared with ratios of emitted species. For example, Fujita et al. (1992) showed that the ratios of ambient CO to NO$_x$ concentrations measured during the morning traffic peak provided an accurate indication of the emission ratios of these species from onroad vehicles in the California South Coast air basin. The goal here is to use measured ambient CO/NO$_x$ ratios obtained throughout the United States to test reported CO and NO$_x$ emissions from onroad vehicles.

Parrish et al. (2002) showed that ambient measurements at carefully selected urban sites accurately reflect the absolute values and temporal trends of the CO to NO$_x$ ratio in onroad vehicle emissions. For CO/NO$_x$ ratios the separation of the influence of onroad vehicle emissions from the influence of other source emissions is of greater concern than for the ambient CO levels discussed in the preceding section. Compared to CO, NO$_x$ from onroad vehicles account for a smaller fraction (35 percent) of the total NO$_x$ emissions, while the two other major sources (offroad vehicles and industrial plus electrical power generation) account for larger fractions (19 percent and 44 percent, respectively). It is important to minimize the confounding influence of these two sources. A four-pronged approach is adopted:
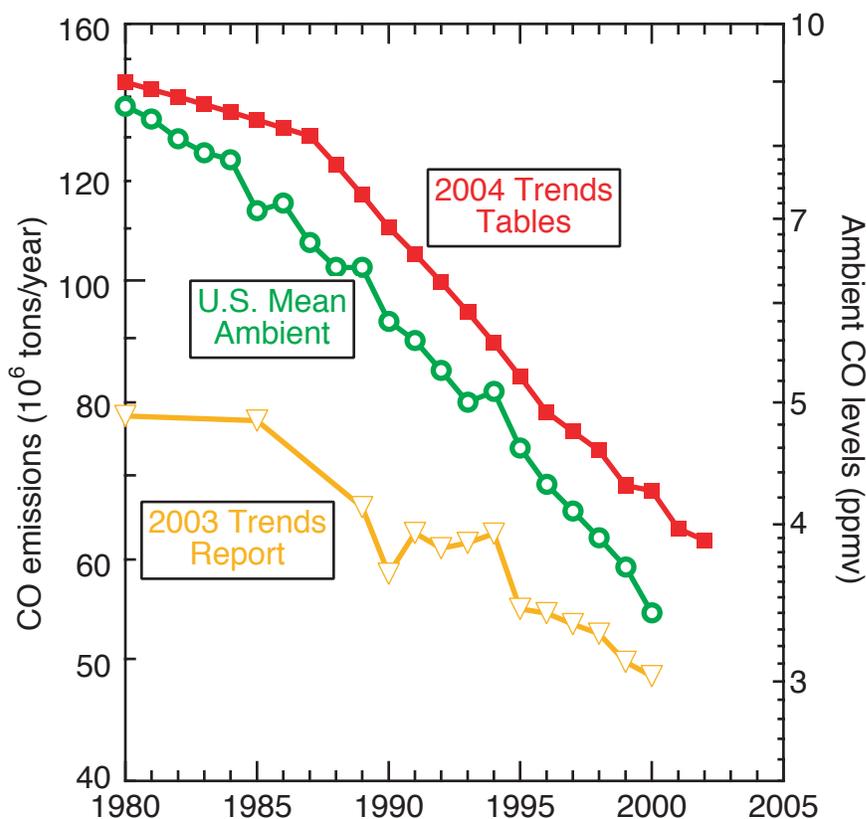
**Figure 7.2. Semi-log plot of national onroad vehicle temporal emission trends.** Two U.S. inventories are compared to observed second-highest annual maximum 8-hr average concentration.

1. Data are considered only from urban areas, where the onroad emissions are localized. In general, the other major $NO_x$ and CO sources are less localized in these areas.

2. Data that avoid very local sources and reflect well-mixed urban emissions are utilized when possible. The goal is to obtain measurements representative of the urban onroad vehicle fleet rather than any particular traffic flow.

3. Data are considered only from the morning onroad vehicle traffic peak, which minimizes several potential problems. First, this is the time of maximum onroad vehicle traffic volume and especially maximum ambient concentrations from those emissions, since they are confined to a shallow mixed layer. Second, this is also likely to be a period of minimum offroad vehicle activity. Third, the influence of industrial and electrical power generation emissions are minimized, because they are predominantly above the morning mixed layer. Finally, this morning period is characterized by low photochemical activity, so the loss of emitted $NO_x$ due to photochemical conversion and deposition processes will minimally perturb the ambient $CO/NO_x$ ratios from those emitted.

4. The $CO/NO_x$ emission ratios are determined from the slope of the correlation between measured CO and $NO_x$ mixing ratios as discussed more fully by Fujita et al. (1992) and Parrish et al. (2002). This analysis has three important attributes. First, transport of regional levels of CO into the urban area does not affect the analysis, because the intercept but not the slope of the correlation is affected by that transport. Second, industry and electrical power generation sources emit little CO, so $NO_x$ from these sources is poorly correlated with CO, and has little influence on the slope. Third, the offroad vehicle

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contributions to CO and $NO_x$ emissions are also poorly correlated, since lawn and garden gasoline engines dominate CO emissions and nonroad diesel engines dominate $NO_x$ emissions; thus, these emissions also have little influence on the slope.

Figure 7.3 shows the CO to $NO_x$ emission ratios from onroad vehicles from the two most recent emission reports discussed in the preceding sections, and compares these inventory ratios to $CO/NO_x$ ratios derived from the five ambient data sets summarized in Table 7.1. All of the ambient data are from the summer, except for the wintertime Boulder study. The Nashville and Boulder results (for clarity this latter site is not included in Figure 7.3) are from single sites selected to sample well-mixed urban onroad vehicle emissions. CO and $NO_x$ at these sites are highly correlated ($r^2 \geq 0.9$), indicating the site selection

was successful. The site in Atlanta, GA has only a short data record (the point in Figure 7.3 represents the average for 1991-2001 August data) with weaker correlations ($r^2 = 0.5$ to $0.8$), which reflect the site's closer proximity to local traffic. The Los Angeles data set combines all August data from eight sites distributed throughout that region. The 1987 result is from Fujita et al. (1992); the later results are from the same sites, except the Pomona, CA site has been substituted for the discontinued Claremont, CA site used by Fujita et al. (1992). Perhaps surprisingly, these CO and $NO_x$ data are highly correlated ($r^2 = 0.8$ to $0.9$), which indicates a highly homogenous onroad vehicle emission mix throughout the Los Angeles region. Finally, the AIRS data set includes all co-located CO and $NO_x$ measurements in the U.S. EPA's AIRS database. Each year includes over 100 primarily urban sites covering the entire country. Each point is equal to the slope of the correlation
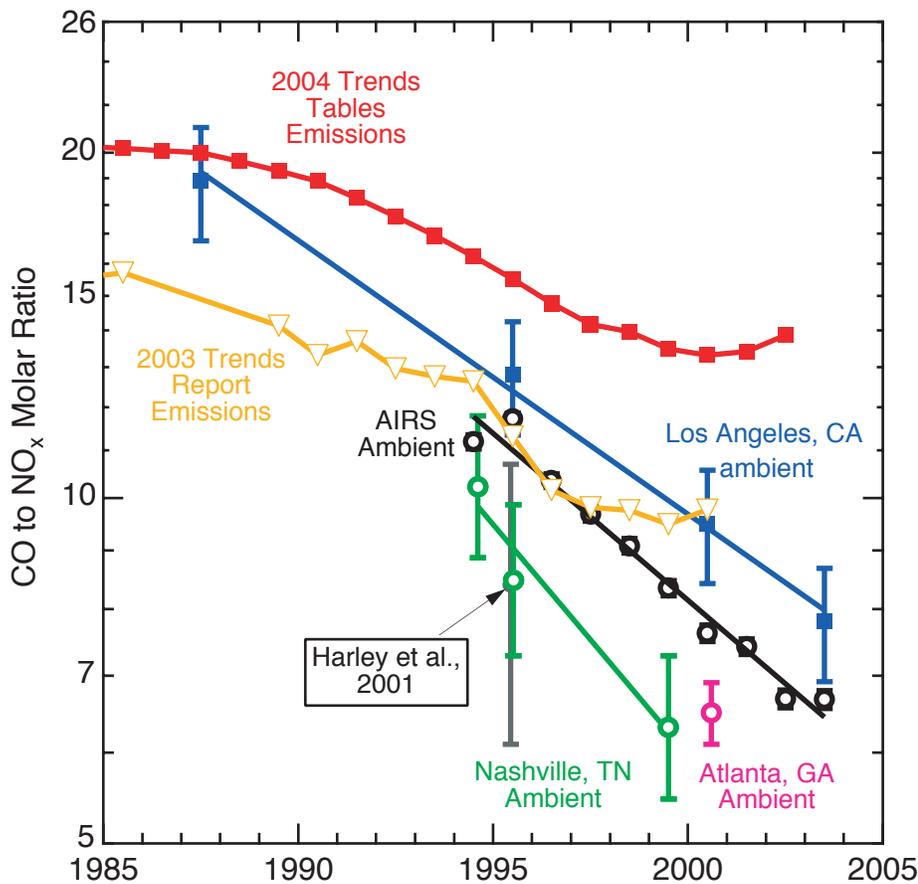


**Figure 7.3. Semi-log plot of temporal trends of CO to $NO_x$ ratio in onroad vehicle emissions.** National emissions from two U.S. inventories are compared to ambient ratios measured in Los Angeles, Nashville, Atlanta and the AIRS network.. Figure based on that in Parrish et al., 2002.

| Table 7.1.  Derived CO/NO$_x$ Emission Ratios During Morning Traffic Peaks (molar ratios). | | | | | |
|---|---|---|---|---|---|
| Location | Measurement period | Ratio in 2000[a] | Temporal trend[a] (%/yr) | r$^2$ | Data Source |
| Los Angeles, CA | 1987-2003 | 9.4 ± 0.7 | -5.5 ± 0.4 | 0.95 | Fujita et al. (1992), CARB[b] |
| Boulder, CO | 1989-1999 | 9.0 ± 1.2 | -6.7 ± 0.5 | 0.94 | Parrish et al. [2002] |
| Nashville, TN | 1994-1999 | 5.7 ± 0.4 | -8.8 ± 1.0 | 0.96 | Parrish et al. [2002] |
| Atlanta, GA | 1999-2001 | 6.5 ± 0.4 | ---- | ---- | SEARCH[c] |
| U.S. Urban | 1994-2003 | 7.9 ± 0.1 | -6.6 ± 0.3 | 0.97 | AIRS[d] |

[a] Values derived from exponential fits as shown in Figure 7.3.
[b] 1995 and later data from CARB website (http://www.arb.ca.gov/adam/cgi-bin/db2www/adamhourly.d2w/start).
[c] SEARCH (Southeastern Aerosol Research and Characterization Study) 2005.  Data downloaded from http://www.atmospheric-research.com/public/index.html.
[d] Data provided by from the U.S. EPA AIRS data base.

between CO and NO$_x$ measurements at all of those sites from July and August for 6:00-9:00 am local time.  Not surprisingly, these data have weaker correlations (r$^2$ = 0.4 to 0.6), reflecting not only the proximity of some sites to local traffic sources, but also regional differences in the average onroad vehicle CO to NO$_x$ emission ratio.

Figure 7.3 and Table 7.1 indicate that there are small regional differences both in the temporal trend, and in the magnitude of the CO to NO$_x$ emission ratio. Noticeably apparent are higher ratios with slower temporal decrease in the Los Angeles area and lower ratios with more rapid decrease in the southeastern U.S.  These patterns could each be compared to the available emission inventory for the respective area.  However, these differences are not great, and comparison to the national emission inventory is used instead.  In Section 7.1.5, the AIRS trend, which represents stations from the entire country and falls in the middle of the observed variations, will be taken as representative of national onroad emissions.

Comparison of the inventory trends with the ambient data trends in Figure 7.3 leads to two conclusions. First, the 2004 Trends Tables emission ratios are significantly higher than found in the ambient data, particularly in more recent years.  The 2003 Trends Report also rises above the ambient trend after 1997.  This indicates that the CO emission estimates are higher and/or the NO$_x$ emission estimates are

lower than can be consistent with the ambient measurements.  These are not small differences; by 2002 they are greater than a factor of 2 for the 2004 Trends Tables.  Second, the temporal trends of the inventory ratios are not as steep as the trend of ambient ratios.  However, the preceding section found good agreement between the temporal trends of the ambient CO levels and the CO emissions in the 2004 Trends Tables.  These two findings indicate that NO$_x$ emission estimates are decreasing too rapidly (or increasing too slowly) to be consistent with the ambient determinations.

Some caveats should be discussed with regard to these conclusions.  First, the error bars shown in Figure 7.3 represent the uncertainty in deriving the slope of the CO/NO$_x$ correlation, but do not include any added uncertainty due to the possibly confounding effects discussed above.  It is not possible at this point to assign reliable confidence limits to the ambient determinations of the onroad vehicle emission ratio, since the magnitude of the confounding effects have not been quantified.  However, the conclusions reached here can be compared with other work.  CRC (2004) recently reviewed results from tunnel studies and remote sensing measurements of onroad vehicle emissions that suggested an overestimate of about a factor of 2 in the MOBILE6 predictions for the CO emissions from onroad vehicles.  However, they also reported measurements of ambient CO/NO$_x$ ratios that implied contradictory conclusions; these ambient

ratios suggested an even larger underestimate in the CO emissions. Consequently, CRC (2004) could reach no firm conclusions regarding the accuracy of the MOBILE6 predictions. Unfortunately the ambient analysis was handicapped by using CO and $NO_x$ data from sensors sited at locations within urban areas that were 3 to 20 km apart, which precluded use of the correlation analysis employed here. The conclusions reached above provide a resolution of the contradiction in CRC (2004), since they are also consistent with an overestimate of about a factor of 2 in the MOBILE6 CO emissions.

## 7.1.4 Comparison of Fuel-Based and Mileage-Based Estimates of Onroad Vehicle Emissions

A fuel-based approach to emission inventory development provides an effective comparison for the mileage-based method used by the U.S. EPA and others. In one example, Harley et al. (2001) developed an inventory for Nashville, TN in 1995 by taking gasoline and diesel fuel sales as the activity factor and determining emission factors expressed as per unit of fuel burned. CO emission factors were determined from infrared remote sensing of over 34,000 vehicles at 13 sites in the urban area. VOC emission factors were estimated from these derived CO emission factors and measured VOC/CO ambient concentration ratios in central Nashville. $NO_x$ emission factors were developed from roadway tunnel measurements made in other U.S. locations. The goal here is to use this comparison to test the accuracy of the estimated magnitude of emissions from onroad vehicles.

In Figure 7.3 the CO/$NO_x$ emission ratio from the fuel-based inventory (Harley et al., 2001) is compared to the ambient ratio discussed in the previous section. The excellent agreement gives us confidence both in the results of the fuel-based emission calculation, and in the validity of directly comparing those ambient concentration ratios with the ratio of the emissions from inventories.

Figure 7.4 compares the results of the fuel-based and U.S. EPA inventories. The U.S. EPA inventory was based on the MOBILE5B emission factor model, which is the modeling basis for the 2000 and 2003

Trends Reports. Thus, the comparison in Figure 7.4 is a test of these Trends Report emissions, but not the 2004 Trends Tables, which are based on MOBILE6. This comparison suggests three conclusions:

1.  There is excellent agreement in the total VOC and $NO_x$ emissions. This comparison increases the confidence in the Trends Reports' estimates of these emissions for 1995.

2.  The U.S. EPA CO emission estimate is about 40 percent higher than the fuel-based estimate. This suggests that the inventory overestimate of the CO to $NO_x$ emission ratio discussed in Section 7.1.3 is at least partially due to an overestimate of the CO emissions as opposed to an underestimate in the $NO_x$ emissions.

3.  Even though the total $NO_x$ emissions agree well, the fraction the U.S. EPA attributed to diesel-powered vehicles is much smaller in the U.S. EPA inventory (25 percent), than is the fuel-based inventory (47 percent). The latest U.S. EPA emission estimates are in closer agreement with the fuel-based inventory. For example, the 1995 nation-wide diesel contribution to $NO_x$ emissions from onroad vehicles is estimated as 43 percent in the 2004 Trends Tables compared to 32 percent in the 2000 Trends Report.

Both the fuel-based and mileage-based approaches are subject to significant uncertainties. Two particular issues that the fuel-based approach must grapple with are (1) the uncertainty associated with fuel sales data and apportioning such data to the study area, and (2) limitations and errors associated with deriving emission factors from measured onroad vehicle emissions at a relatively small number of sites that may not be representative of the complete driving cycle, and likely may miss higher CO emissions associated with "cold-starts" of gasoline engines. Consequently, examination, testing and modification of both emission inventory approaches must continue until they agree.

The experience in comparing fuel-based and VMT-based emissions in California provides an example for the national inventory to emulate. In this work, Singer and Harley (2000) developed a fuel-based inventory for the Los Angeles area for the summer of 1997. Their emissions were higher than the then
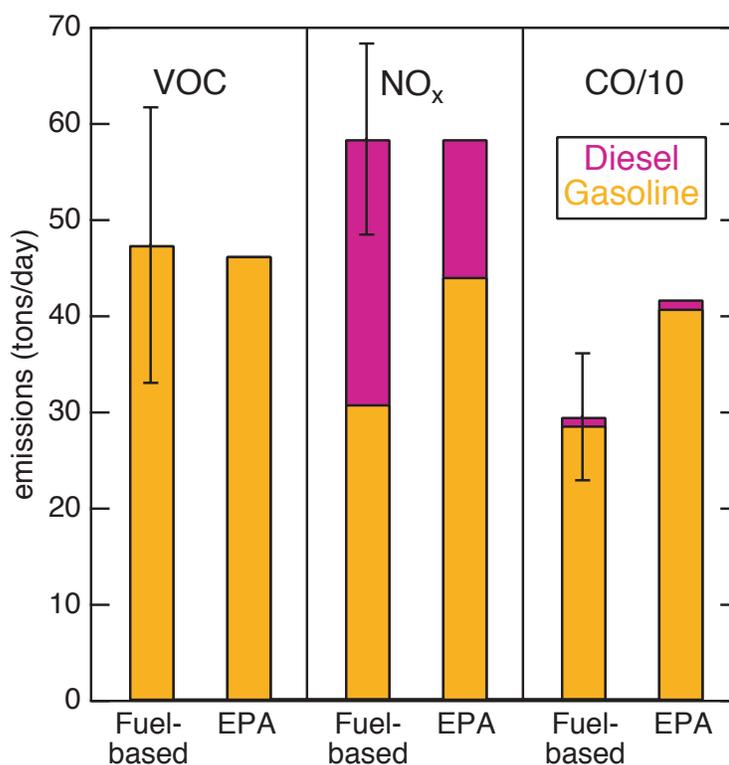
**Figure 7.4. Comparison of fuel-based emission inventory for Nashville in 1995 with the U.S. EPA emission inventory for that county** (Harley et al., 2001). CO emissions are divided by 10 to include on the same ordinate. The error bars indicate the estimated uncertainty of the total fuel-based emissions.

current California mobile emission model (EVEI 7G) estimates by factors of about 2.4 for CO and 3.5 for VOC. However, an improved California model (MVEI 2002) now has come into agreement with the Singer and Harley (2000) estimates (CARB, 2002). It is recommended that high priority be extended to these reconciliation efforts for the NEI and for other regions of the country.

### 7.1.5  Reconciliation of Estimated Onroad Vehicle Emissions with Ambient Measurements

The three preceding sections have compared estimated emissions to ambient measurements and compared two inventories developed from different approaches. These comparisons have identified inconsistencies that indicate significant errors, either in the inventories or in the ambient measurements and/or their interpretation. Here, a process of

identifying the errors that underlie the identified inconsistencies is presented, with the goal of guiding improvements in emission inventories as well as their evaluation through ambient measurements. The goal of this section is to suggest changes in the onroad vehicle emission estimates that are necessary to reconcile them with the ambient measurements and the fuel-based inventory.

Figure 7.5 shows inferred onroad vehicle emissions for $NO_x$ and CO (black symbols) for the 1990-2000 period. These inferred emissions are consistent with all of the ambient data discussed above, and are derived from four assumptions:

1.  Consistent with the fuel-based inventory discussion in Section 7.1.4, the 1995 $NO_x$ emissions from the 2003 Trends Report are assumed to be accurate. The inferred $NO_x$ emissions in 1995 are set equal to the value for that year from Table A4 of that report (solid black circle in upper panel of Figure 7.5).

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2.  Also consistent with the fuel-based inventory discussion in Section 7.1.4, the 1995 CO emissions from the 2003 Trends Report are assumed to be overestimated by 40 percent, not only in Nashville, but nationwide. The inferred CO emissions in 1995 are set equal to the value for that year from Table A2 of that report divided by 1.4 (solid black circle in lower panel of Figure 7.5).

3.  Consistent with the discussion in Section 7.1.2, CO emissions are assumed to have decreased by 4.9 percent/year, the rate of decrease of the ambient CO levels for 1985-2000. Extrapolating this rate of decrease backward and forward in time for five years from 1995 gives the inferred CO emissions for all years (open black circles in lower panel of Figure 7.5).

4.  Consistent with the discussion in Section 7.1.3, the CO to $NO_x$ emission ratio is assumed to have decreased by 6.6 percent/year, the rate derived from the nationwide AIRS data set. This implies an increase in $NO_x$ emissions of 1.9 percent/year.
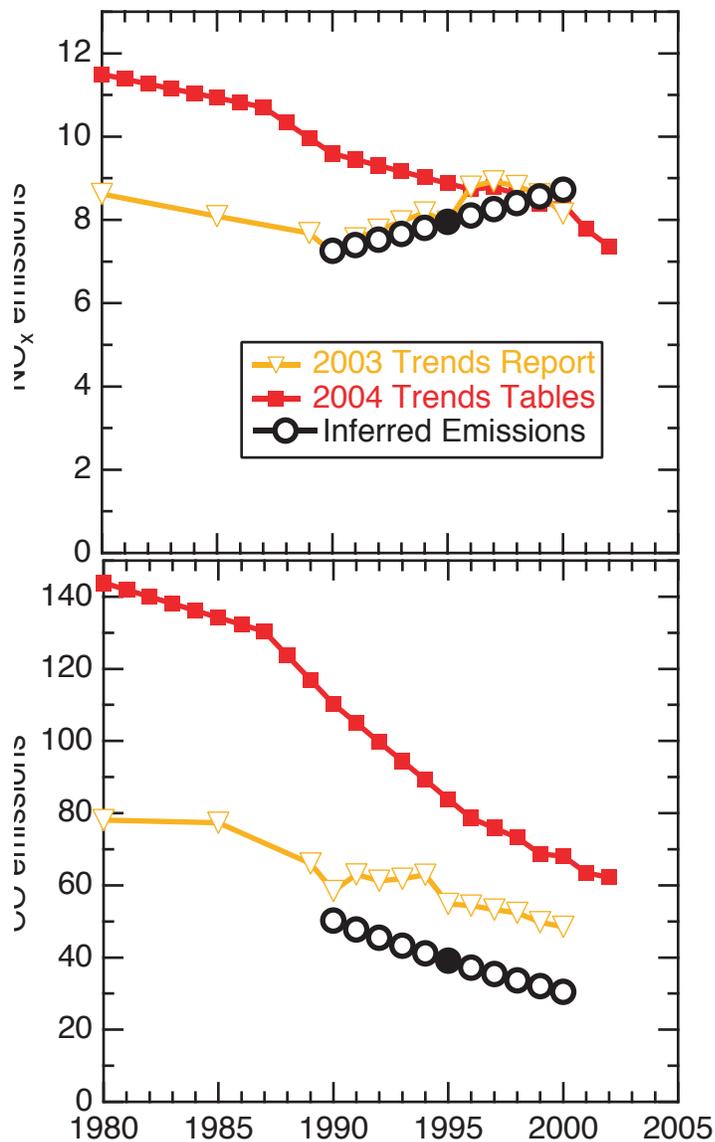


**Figure 7.5. National onroad vehicle emissions from the two most recent U.S. inventories in Figure 7.1 compared to the emissions inferred from ambient measurements.** Units are $10^6$ tons/year.

Extrapolating this rate of increase backward and forward in time from 1995 gives the inferred $NO_x$ emissions for all years (open black circles in upper panel of Figure 7.5).

If these inferred emissions are accurate, then these results imply that errors exist in the onroad vehicle emission estimates from the Trends data. Two apparent errors are particularly notable. First, CO emissions in the 2004 Trends Tables may be overestimated by about a factor of 2 for 1990-2000, while the 2003 Trends Report may overestimate the emissions by a smaller factor averaging about 40 percent. Second, the temporal trend of $NO_x$ emissions is poorly defined by the emission inventories. The 2003 Trends Report shows an increase averaging 2.8 percent/year from 1990-1997 followed by a decrease, while the 2004 Trends Tables show a continuing decrease averaging 1.4 percent/year for 1990-2000. Figure 7.1 shows that the temporal trend of the $NO_x$ emissions has been revised between each successive emission report, always with higher estimates for the 1990-2000 period. However, despite these divergent temporal trends, the 2003 Trends Report values are within 9 percent of the inferred $NO_x$ emissions for all years, and the 2004 Trends Table values are within 20 percent of the inferred $NO_x$ emissions for all years after 1992.

No substantial inconsistencies have been identified in the VOC onroad vehicle emissions. The fuel-based and the U.S. EPA inventory, consistent with the 2003 Trends Report agreed very well for 1995 in Nashville (Figure 7.4). The 2004 Trends Tables estimates for years after 1993 are no more than 18 percent higher than the 2003 Trends Report (Figure 7.1). The temporal trend of the VOC road emissions for 1985-2000 in the 2004 Trends Tables corresponds to an average decrease of 5.9 percent/year, which is in reasonable agreement with the decrease in CO emissions of 4.9 percent/year assumed above. This agreement between the temporal trends of CO and VOC onroad vehicle emissions is expected from onroad vehicle emission studies (Parrish et al., 2002). CRC (2004) found good agreement of ambient VOC/$NO_x$ ratios with inventories in the 1998-2000 time period, which is in accord with the separate analyses presented here for VOC and $NO_x$.

Future steps in the process to reconcile the top-down tests with emission inventories ideally will include feedback from inventory developers regarding the validity of the suggested inventory changes and evaluation of errors in the ambient measurements and/or their interpretation. With regard to this last point, the rate of increase in the inferred onroad vehicle $NO_x$ emissions is derived from the difference between the rates of decrease of two temporal trends (ambient CO levels and ambient CO to $NO_x$ ratio) determined from measurements. This difference between two measurement-derived quantities may be a significant source of uncertainty in the inferred emissions discussed here.

In Figure 7.5, the inferred increase in $NO_x$ onroad vehicle emissions is in reasonable accord with the trend in the 2003 Trends Report. This increasing trend is not present in the 2004 Trends Tables. It may be fruitful to investigate if the 2003 Trends Report is more accurate than the later report and the cause of the disappearance of the increasing $NO_x$ emission trend between the reports. This investigation may focus on the inconsistency in the apportionment of $NO_x$ emissions between gasoline- and diesel-fueled vehicles identified in the inventory comparison in Figure 7.4. Through the 1990s, emission factors for diesel vehicles remained approximately stable, while diesel fuel consumption increased. As noted by NRC (2000), $NO_x$ emissions from heavy-duty diesel vehicles were underestimated in the then-current MOBILE model, and $NO_x$ (as well as PM) emission rates were highly uncertain.

One implication of the decreasing trend in CO emissions from onroad vehicles deserves attention. If the trend in Figure 7.5 has continued to 2002 and if the other CO emissions for that year in the 2004 Trends Tables are accurate, then the onroad vehicle contribution to the total U.S. CO emissions has declined to about 40 percent in 2002. This implies that other emission sources (which may be even more uncertain) are accounting for a majority of the total inventoried CO emissions. For example, emissions from nonroad vehicles and engines would nearly equal those of onroad vehicles. Thus, emissions from sources other than onroad vehicles should be an increasing focus for future inventory improvement and uncertainty analyses.

### 7.1.6 Evaluation of VOC Speciation in Onroad Emission Inventories

Evaluation of ambient VOC measurements under appropriate conditions can provide critical tests of VOC speciation. Benzene and acetylene are particularly appropriate for testing onroad vehicle emission for three reasons. First, they are primarily emitted from onroad vehicles, so ambient urban levels do provide information regarding this source. Second, they react slowly in the atmosphere with lifetimes on the order of ten days, so their interrelationship is not affected by removal in the atmosphere. Third, both of these hydrocarbons are in the top ten in terms of ambient urban levels, so quantification of their concentrations is not limited by instrumental sensitivity. The goal of this section is to use the measured ratio of ambient concentrations of these species to test the ratio of these species in onroad vehicle emission inventories.

Fortin et al. (2005a) show that the benzene to acetylene ratio is remarkably invariant over large regions of the country in any given year, and that this ratio exhibits long-term trends in response to VOC emission control measures (Figure 7.6). Before 1994, the ratio increased slowly due to the preferential removal of acetylene by automotive catalytic converters, which penetrated the vehicle fleet during this period. Specific benzene control measures were begun in 1994 in response to the 1990 Clean Air Act Amendments, which have substantially reduced the ratio in recent years. These ratios and their trend can be compared to the VOC speciation in emission inventories.
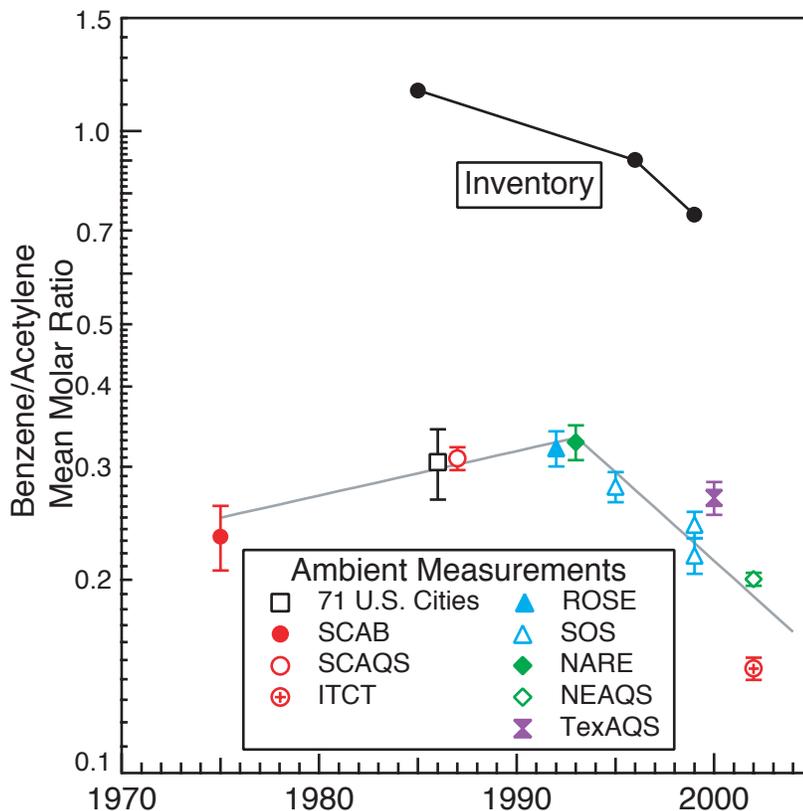


**Figure 7.6. Observed trends in the mean ambient benzene to acetylene ratio from field study data as a function of year on a semi-log plot.** The colors of the symbols indicate geographic location: Average of 71 U.S. urban areas (black), California (red), southeast (blue), northeast (green), and Texas (purple). The error bars indicate the 95 percent confidence limit of the mean. The gray lines indicate estimated ambient trends before and after 1993. The inventory ratios are from Table 7.1. (Figure closely follows that of Fortin et al. [2005a].)

Total national benzene and acetylene emissions from three recent emission inventories are given in Table 7.2. The corresponding ratios are plotted in Figure 7.6. The NEI 1996 and 1999 numbers were obtained by applying the SPECIATE software to the respective NEI. The 1996 number agrees to within 10 percent with the 1996 National Toxic Air Pollutant inventory for benzene (http://www.epa.gov/ttn/atw/nata/). Interestingly, the National Air Quality and Emissions Trends Report, 1999 states that the average annual ambient levels of benzene decreased by 40 percent from 1994-1999, but this decrease is not reflected in the benzene emission numbers.

The comparison between the ambient and inventory ratios is quite poor. The inventory values are a factor of 3 to 4 higher than the ambient measurements, and the temporal trends are not clearly in agreement. The ambient measurements must be considered to accurately reflect average emissions. The measurements are from at least seven different research groups and span most of the country. Benzene and acetylene react similarly and so slowly that average emission ratios are not significantly altered before measurement. Disagreements must reflect biases in the inventory ratios. Although the recent trend in the inventory appears to parallel the ambient trend, it is for the wrong reasons. The ambient ratio is believed to have decreased due to decreasing benzene emissions, but Table 7.2 shows that in the inventories benzene emissions have remained nearly constant while the acetylene emissions have increased, resulting in a decreasing ratio.

In conclusion, the VOC speciation in the NEI compared to ambient measurements as tested by these example species shows a difference of factors of 3 to 4, the temporal trend in the inventory emissions is not consistent with the observations, and the NEI does not reflect trends in ambient concentrations that are discussed in the Trends Report. There is a critical need for a re-evaluation of the VOC speciation in the NEI. Correctly interpreted, reliable ambient concentration measurements must be one of the important guides for this re-evaluation. This conclusion is in accord with the finding by NRC (2000) that the database, upon which the SPECIATE system is based, is now out of date, especially for mobile-source emissions.

## 7.2 EVALUATION OF POWER PLANT EMISSIONS IN THE UNITED STATES

Power plant emissions account for a major share of $NO_x$, $SO_2$ and $CO_2$ emissions, and are responsible for some of the highest concentrations of these species encountered in the ambient atmosphere. In contrast to onroad vehicle emissions, there are a great many detailed, hourly emission data available, because generally these emissions are measured by CEMS (see Sections 4.7.4 and 6.1.3). These CEMS are required by the U.S. EPA Acid Rain Program, and are maintained to high standards, with daily zero and span calibration checks, routine multipoint calibrations, and regular independent accuracy audits. Accurate emission inventories should be available

| Table 7.2. Benzene and Acetylene Emissions ($10^5$ moles/hour).[a] | | | |
|---|---|---|---|
| **Species** | **NAPAP 1985** | **NEI 1996** | **NEI 1999** |
| Benzene | 10.69 | 4.08 | 3.98 |
| Acetylene | 9.24 | 4.53 | 5.38 |
| Ratio | 1.157 | 0.901 | 0.740 |
| [a]The emissions are given in units of moles/hour to ease direct comparison of inventories and the derivation of ratios. For comparison 1 mole/hour corresponds to 0.251 tons/year of acetylene and 0.753 tons/year of benzene. There are subtle differences in the units: 1985 are annual average hourly emissions; 1996 are hourly average for ozone season workday; and 1999 are hourly average for all summer days. These differences are likely small. The emissions exclude all fire emissions, because the ambient measurements were not significantly affected by fire emissions. The 1985 benzene emissions include halobenzenes. | | | |

simply from the integration of these CEMS data over the time period of interest. In this section, the reported power plant emissions are examined for internal consistency over the past two decades, and the consistency of CEMS data with aircraft measurements is investigated.

### 7.2.1 History of Temporal Trends of Power Plant Emissions.

This section examines the history of emission trend estimates for power plants in a manner similar to that presented in Section 7.1.1 for onroad vehicle emissions. The aim is also the same: to determine if the estimated trends are converging to more precisely defined values, or if there is a significant element of scatter in the estimates that may indicate fundamental uncertainties in the estimation methods.

Figure 7.7 presents inventoried emissions of $NO_x$ and $SO_2$ from fuel combustion in electrical utilities. The numbers come from five of the six references investigated in Section 7.1.1. (The 1990 Trends Report does not give emissions from power plants separately from other point sources). It is clear here that there has been little variation in the emission estimates for any given year, with only the $NO_x$ emissions in the 1995 Trends Report significantly different (as much as 19 percent higher) than the other estimates. This test gives no indication of any important uncertainties in the estimated trends of power plant emissions.

### 7.2.2 Tests of CEMS Data for Power Plant Emissions

Transects of power plant plumes by aircraft capable of making rapid measurements of the emitted species provide a means of deriving emission fluxes from ambient measurements. These measurements can be directly compared with the CEMS data collected at the time of emission of the

sampled plume. The primary goals in this section are (1) to test the consistency of the available CEMS data with aircraft flux measurements, and (2) to test the integration of CEMS data into annual inventories.

In principle, the absolute flux of a species emitted from a source can be directly determined from aircraft measurements of its concentration in the downwind plume. The flux is equal to the wind speed at the time of emission multiplied by the integral of the species concentration over the cross section of the
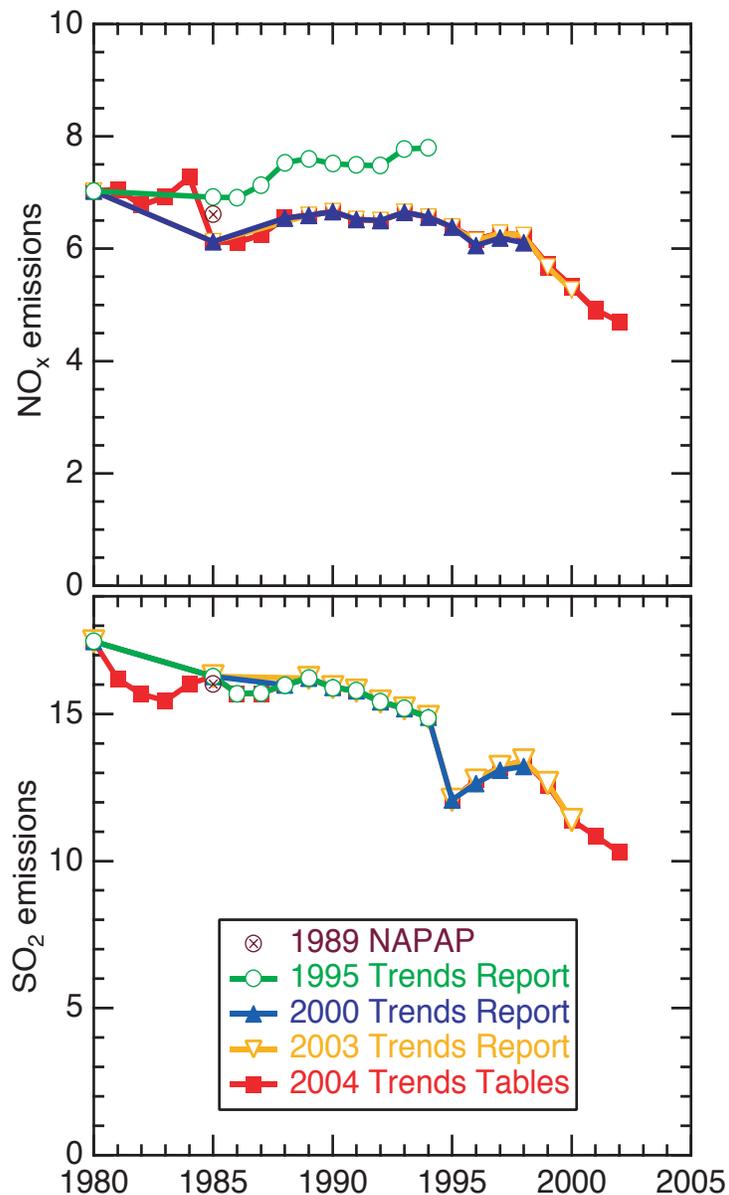


**Figure 7.7. National power-plant emissions from five U.S. inventories in units of $10^6$ tons/year.** The dates indicate the year of publication of the inventory report.

plume perpendicular to that wind direction. These concentration data can be collected during aircraft transects of the plume. In practice, collection of data of adequate spatial resolution and coverage to allow accurate integration over the plume cross section is daunting. Generally the plume flux determinations are carried out under favorable conditions that allow significant simplifications (see Ryerson et al., 1998, and references therein).

The favorable conditions for aircraft plume flux determinations are those where three approximations can be made: (1) the plume is confined to the PBL, (2) the plume is well-mixed over the depth of the PBL, and (3) the wind speed and direction in the PBL are constant from time of emission to measurement. Under these conditions the flux of species m can be calculated from wind and concentration measurements collected in a single plume transect:

$$\text{flux}_m = v \bullet \cos\alpha \int_0^{z_0} n(z)dz \int_{-y}^{+y} X_m(y)dy \quad (7.1)$$

Here $v$ is the wind speed and $\alpha$ is the deviation of the aircraft transect from perpendicular to the wind direction, $n(z)$ is the number density of air as a function of $z$, the height above ground, $z_0$ is the PBL height, and $X_m(y)$ is the mixing ratio enhancement above background of species $m$ as a function of $y$, the cross plume distance. Under optimal conditions the uncertainty in this calculation can be as low as plus or minus 20 percent. Figure 7.8 shows data collected under such favorable conditions. The fluxes derived from Equation (7.1) for $NO_x$, $SO_2$ and $CO_2$ agree very well with tabulated CEMS data. (The $NO_y$ measurements plotted represent the sum of all oxidized nitrogen species, which includes not only the emitted $NO_x$ that remains in the plume, but also any species, such as $HNO_3$ and PAN, that are produced by photochemical oxidation of $NO_x$ between emission and measurement.)

Under conditions where one or more of the above approximations fail, it is still possible to determine

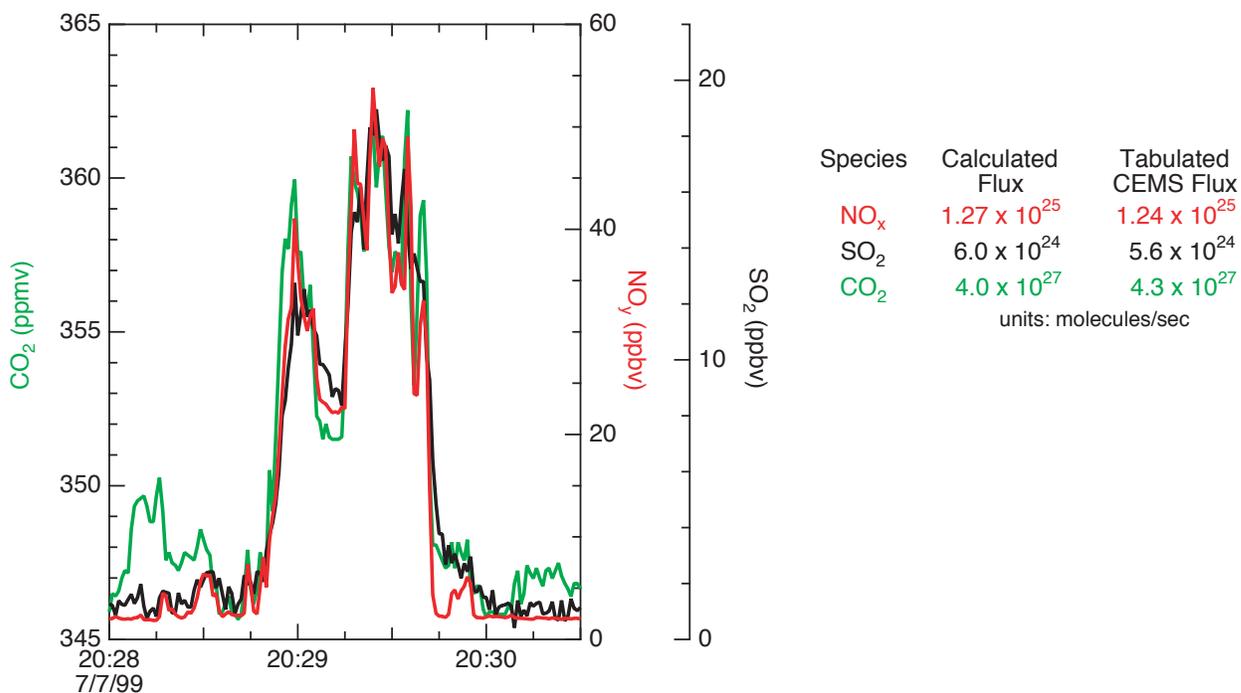| Species | Calculated Flux | Tabulated CEMS Flux |
|---|---|---|
| $NO_x$ | $1.27 \times 10^{25}$ | $1.24 \times 10^{25}$ |
| $SO_2$ | $6.0 \times 10^{24}$ | $5.6 \times 10^{24}$ |
| $CO_2$ | $4.0 \times 10^{27}$ | $4.3 \times 10^{27}$ |

units: molecules/sec

**Figure 7.8. One-second average data collected during a 2.5 minute transect of the Thomas Hill coal-fired power plant in Randolph County, MO during the 1999 Southern Oxidant Study.** This transect was conducted 20 km downwind of the plant, approximately 1.5 hours after emission. The fluxes of the three emitted species calculated from Equation (7.1) are compared to those reported from CEMS measurements.

at least the ratio of the fluxes of two emitted species, even from only a partial transect of the emission plume. The slope of the correlation between the concentrations of two species is equal to the ratio of their fluxes. For example, for the data of Figure 7.8 the slope of $NO_y$ versus $CO_2$ is $3.3 \times 10^{-3}$ with an $r^2$ of 0.93; the corresponding slope for $SO_2$ versus $CO_2$ is $1.14 \times 10^{-3}$ with an $r^2$ of 0.89. These slopes agree well with the ratios of the CEMS emissions: $3.3 \times 10^{-3}$ and $1.30 \times 10^{-3}$, for $NO_x/CO_2$ and $SO_2/CO_2$, respectively. These derived slopes are not affected by failure of any of the three approximations listed above.

Finally, conservation of the emitted species in the plume from emission to measurement is required to determine an absolute emission flux. This conservation implies negligible loss by any mechanism, such as in-situ chemical removal, surface deposition or venting of the plume out of the PBL. The determination of flux ratios is not sensitive to boundary layer venting, but is affected by different rates of removal of the two species by either chemical removal or surface deposition.

Nearly 50 such plume studies on over 30 CEMS-equipped power plants during field studies in 1995, 1997, 1999, 2000, and 2002 have been conducted (Ryerson et al., 1998; Neuman et al., 2004 and references therein.) Fortin et al. (2005b) have summarized all of these studies and their results are shown in Figure 7.9. Figure 7.9(a) compares the flux ratios of $NO_x$ to $CO_2$ and $SO_2$ to $CO_2$ derived from CEMS to those derived from aircraft transects. On average these flux ratios agree within the estimated uncertainty of the ambient determination (plus or minus 20 percent), although there are occasional significant discrepancies. Figure 7.9(b) compares the fluxes measured for $NO_x$, $SO_2$ and $CO_2$, with those derived from the CEMS data. Agreement on average is again within plus or minus 20 percent, again with occasional significant discrepancies. These comparisons indicate that emission fluxes of $NO_x$, $SO_2$ and $CO_2$ from power plants derived from CEMS measurements are highly accurate.

The significant discrepancies between the CEMS and aircraft determinations are generally due to the inherent uncertainty of comparing an in-situ stack measurement with the aircraft-based measurement.

However, occasional inaccuracies in the CEMS data are indicated. At those times the aircraft sequentially sampled plumes from two or three closely spaced plants on a single transect, and then repeated that transect two or three times. Consistent, good agreement between the aircraft measurements and the CEMS data was found for some or all of the emitted species from one or two of the plants and consistent, poor agreement for one or more species from a different plant. These observations indicate inaccuracies in the CEMS data in those specific instances.

Both the flux ratios and the absolute emission fluxes from CEMS agree equally well, on average, with those derived from ambient aircraft measurements. It is notable that the absolute flux determinations (which depend on the measured total stack flow in the CEMS determinations) are as accurate as the determination of the ratio of fluxes (which are independent of the total stack flow). However, the absolute determinations shown in Figure 7.9(b) do show larger scatter, but this is partly or wholly due to the reduced precision of the absolute flux determination by aircraft.

The preceding discussion concludes that aircraft flux measurements of power plant emissions are consistent with hourly CEMS data, adding confidence to both methods. The question remains if these short-term measurements are accurately integrated into annual emission inventories. As a check, the 1999 CEMS data for $NO_x$ and $SO_2$ for seven power plants in five states were integrated. On average these integrals agreed with the values in Version 3 of the 1999 NEI to within 1 percent, and the largest discrepancy was 4 percent. These small differences simply may be due to differences in the method of handling missing data. Finally, the sum of all of the power plant emissions in Version 3 of the 1999 NEI was verified to be consistent with the values listed in the 2004 Trends Tables for fuel combustion in electric utilities.

In contrast to the accurate CEMS-derived emissions, CO emissions from power plants are generally estimated from emission factors appropriate to the burner technology and type and amount of fuel consumed. Nicks et al. (2003) have observed that power plants, particularly those fueled by lignite
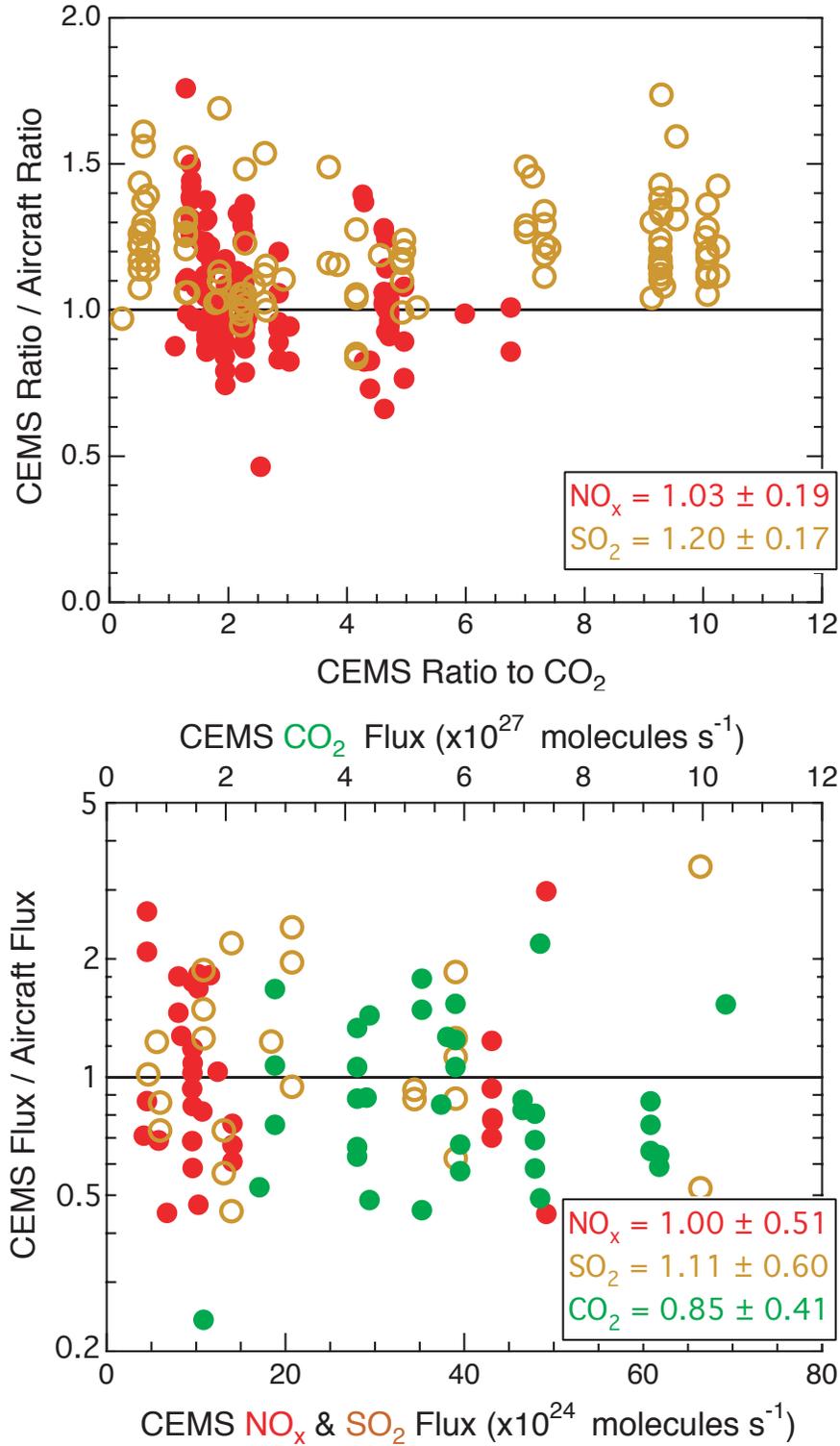
**Figure 7.9. Power-plant emission fluxes from CEMS data compared to those determined from aircraft plume transect measurements.** (a) Emissions of $NO_x$ and $SO_2$ ratioed to those of $CO_2$. (b) Absolute fluxes of all three species. The annotations give the geometric average and standard deviations for the color-coded ratios.

coal, but including one gas- and sub-bituminous coal plant, can emit CO at rates more than a factor 10 higher than inventoried. Nevertheless, power plants still constitute only a minor fraction of total anthropogenic CO emissions.

In summary, power plant emissions based upon CEMS data are highly accurate from hourly to annual average time scales. However, the interpretation of annual average emissions must proceed with caution since the CEMS data indicate that emissions from most power plants vary on all time scales from hours to months to years. Consequently detailed photochemical models should include the hourly CEMS emission data in order to accurately simulate these point source emissions effects on ozone and aerosol formation downwind.

## 7.3 EVALUATION OF EMISSIONS FROM TEXAS PETROCHEMICAL FACILITIES

The greater Houston, Texas, metropolitan area is distinguished by the largest concentration of petrochemical industrial facilities in the United States. Further, Houston is noted for some of the highest present-day ambient ozone concentrations routinely encountered in the continental United States. Hourly averaged ozone concentrations measured at surface sites in the area can exceed 200 ppbv during severe episodes. However, photochemical models based on existing emission inventories are not able to accurately reproduce these high ozone levels. The Texas Air Quality Study (TexAQS 2000) was conducted to develop a comprehensive understanding of these extreme ozone episodes.

During the TexAQS study, aircraft measurements of plumes (see Section 7.2.2) emitted from the petrochemical industrial facilities established that these emissions were responsible for the extreme ozone episodes (Ryerson et al., 2003; Wert et al., 2003). Strongly elevated concentrations of $NO_x$ and reactive VOCs simultaneously present are required for rapid formation of high levels of ozone. $NO_x$ emissions from a large petrochemical facility can approach those from a large electric power plant. These $NO_x$ emissions are co-located with large

emissions of reactive VOCs, primarily ethene and propene, released from the petrochemical processes. Thus, conditions for high ozone formation rates are routinely found in the $NO_x$- and VOC-rich plumes from the petrochemical industrial facilities.

The failure of previous modeling efforts to reproduce the observed extreme levels of ozone was traced to a very large underestimate of alkene emissions from the petrochemical facilities. Measurements established that the alkene emissions were generally as large or larger than the $NO_x$ emissions from the petrochemical complexes. However, alkene emissions derived from the previous inventory were smaller by factors of 10 to 100. Photochemical modeling using VOC emissions scaled up to resolve this discrepancy accurately reproduced the observed concentrations of ozone. These models also accurately predicted the concentrations of other photochemical products, in particular formaldehyde, which is directly produced from the alkenes (Wert et al., 2003). Thus the very high ozone levels observed in Houston downwind of petrochemical plants can be explained by underestimated alkene emissions.

The cause of the underestimate of the alkene emission inventory is poorly understood. One of the major goals of the planned TexAQS 2006 study is to determine the source of the very large reactive VOC emissions from within the petrochemical facilities. However, one aspect of these emissions is clear; the observed discrepancy was generally consistent over all of the facilities sampled during the four-week, August-September, 2000 period of the study. Investigation indicated that the observed discrepancies could not be attributed to reported upset or other transient conditions. Since emissions during startups, shutdowns, and malfunctions are not normally reported in emission inventories, and since emissions from these operations can be significant, these situations need to be addressed in emission inventories.

Allen et al. (2004) have evaluated the variability of alkene emissions, and point out that frequently a single source within a complex can dominate that complex's emissions, and can even approach the annual average of the inventoried emissions for the entire Houston area. This variability is an important feature of these emissions that must receive due

consideration in photochemical modeling. However, Allen et al. (2004) discuss this variability in relation to the tabulated emission inventories. If the variability were compared to the emissions scaled up to match the observations discussed above, its significance would be much reduced.

The findings discussed above promise substantial economic benefits for the Houston area. Prior to the TexAQS 2000 study the state had devised a strategy to result in compliance with the ozone standard and avoid federal sanctions. Based on existing emission inventories, reduction of point source $NO_x$ emissions by 90 percent were required among other control measures. Following the discovery of the large alkene emissions less stringent $NO_x$ reductions, combined with reductions in these alkene emissions, were selected as an effective strategy to meet the air quality standards. This strategy could have reduced economic impacts. A study sponsored by local interest groups (Tolley and Smith, 2001) concluded that ten years after implementation, a 90 percent reduction in $NO_x$ emissions would result in 65,000 fewer jobs and a $9 billion smaller regional economy compared to a 79 percent $NO_x$ reduction strategy that allowed emissions trading. Even when the costs of VOC controls are included, the revised control strategy (which was enabled and supported by the revised emission inventory) resulted in considerable annual savings compared to the original $NO_x$-only alternative.

MARAMA (2003) have provided evidence that the Houston findings are relevant to other regions of the country. They report that high levels of alkenes are observed in plumes downwind of petrochemical facilities along the U.S. mid-Atlantic Coast. These plumes also contained substantially elevated ozone levels.

# 7.4    SOURCE APPORTIONMENT FROM CHEMICAL MASS BALANCE

Receptor methods for source attribution are based on the interpretation of measured ambient concentrations of species to infer sources and to quantify the contributions of these sources to the ambient concentrations. These methods have been extensively reviewed by Watson et al. (2001) for VOC emissions and in Chapter 7 of NARSTO's PM Assessment (NARSTO, 2004). The CMB approach relies upon fitting measured concentrations of ambient species to a linear combination of source profiles. Each source profile defines the relative abundance of the measured species in the emissions from that source. Source profiles may be derived from direct measurements of the composition of the source emissions, or from statistical analyses of the ambient measurements themselves (see e.g. Henry et al., 1994). The CMB approach to source apportionment has provided important evaluations of inventories.

Watson et al. (2001) conclude from their review of CMB analyses that gasoline-related sources (vehicle exhaust and evaporation) generally contribute up to 50 percent or more of the ambient VOC, similar to or larger than their proportions in emission inventories. In contrast, coatings and solvent contributions were found to be much lower than attributed in emission inventories.

One illustrative example presented in the NARSTO PM assessment discusses the relative contribution of $PM_{2.5}$ sources in Denver, CO derived from a chemical mass balance analysis of ambient measurements. (Section 6.2.1 discusses CMB and other receptor modeling techniques in more detail.) The CMB technique derives the contribution from secondary PM formation as well as emissions from primary sources. The relative contributions of the primary sources are compared with those included in the corresponding emission inventory. The comparison found substantial discrepancies. Compared to the CMB approach, the inventory:

- Showed nearly twice the fractional contribution from fugitive dust emissions

- Underrepresented cold start gasoline vehicle exhaust, which makes a substantial contribution in the CMB analysis

- Underrepresented high emitter (i.e., poorly maintained) gasoline vehicles.

The inventory indicated that diesel emissions should have been over three times those of gasoline vehicles, while the CMB analysis showed the ratio of gasoline

vehicle to diesel emissions to be just the opposite. This study again underscores the importance of assessing emission inventories through comparison with ambient measurements.

## 7.5 INVERSE MODELING APPLICATIONS

Section 6.2.2 discusses inverse modeling as one of the evolving tools that will help to improve emission inventories. A study that evaluated the U.S. emission inventory for $NH_3$ provides an illustrative example of the application of this tool. It is an excellent example of the feedback that must occur between emission inventory developers and top-down tests of the inventories; in this case large initial discrepancies have been resolved.

Gilliland et al. (2003) used measurements of both precipitation-weighted $NH_4^+$ wet concentration and ambient $NH_x$ ($NH_3 + NH_4^+$) as bases for inverse modeling to test the accuracy of the U.S. 1990 NEI estimates of $NH_3$ emissions in the eastern United States. Both bases gave a consistent conclusion; i.e., the annual average emissions in the NEI should be 25 to 30 percent lower and should have a strong seasonal cycle. The NEI itself does not specify any seasonality, which has to be introduced via an emission processing model.

A notable feature of this study is that predictions for aerosol $NO_3^-$ (a quantity not included in the inverse modeling optimization) were much improved when the model incorporated the reduced $NH_3$ emissions. This improvement greatly increases the confidence that can be placed in the conclusions of the inverse modeling procedure.

A cautionary note for inverse modeling procedures is that they implicitly assume that the models correctly predict all observed parameters, and any disagreements between measurements and model results are assigned to problems in emission inventories. In this example study, Gilliland et al. (2003) investigated where problems in the model could possibly be contributing to the disagreements; they concluded that there were two critical areas of model uncertainty: total model precipitation and the $NH_3$ dry deposition.

Subsequent work involving both further bottom-up, process-based emission inventory development (Pinder et al., 2004) and inverse modeling has led to a convergence of the two approaches (Gilliland et al., 2005a,b; Pinder et al., 2005). The consensus picture that emerged is ammonia emissions with an approximately 25 percent larger seasonal amplitude than originally proposed by Gilliland et al. (2003), primarily because of even larger decreases in winter emissions. The bias in the 1990 annual NEI inventory has been corrected in the new 2001 NEI inventory, with only an 8 percent increase in the annual 2001 emissions suggested by the inverse modeling results. These studies represent a successful example of feedback from top-down emission studies providing guidance for the refinement of bottom-up inventories.

## 7.6 SUMMARY AND CONCLUSIONS

This chapter has illustrated a number of techniques that utilize ambient measurements to test emission inventories. These top-down tests have reached some conclusions regarding important current emission inventories:

1. Short-term, i.e. hourly, and longer-term average power-plant emission inventories based upon CEMS measurements are generally accurate to better than plus or minus 20 percent. In a few cases significant disagreements between the aircraft measurements and the CEMS data have been observed. These are attributed to the inherent uncertainty of comparing an in-situ stack measurement with an aircraft based measurement and to occasional inaccuracies in the CEMS data.

2. The U.S. onroad vehicle emission inventories have improved substantially in the last decade; however, they may have serious shortcomings. The most recent tabulations (the 2004 Trends Tables based upon the MOBILE6 model):

   • Accurately estimate $NO_x$ emissions for recent years, but indicate a decreasing temporal trend through the 1990s, while top-down evaluations (and previous Trends

Reports) indicate an increasing temporal trend over that period.

- More accurately reproduce the apportionment of $NO_x$ emissions between gasoline and diesel-powered vehicles than did previous Trends Reports.

- Accurately capture magnitude and temporal trend of VOC emissions. However, speciated VOCs from MOBILE6 may be inaccurate by factors of 3 or more, depending on the constituents.

- Accurately capture the temporal trend of CO emissions, but may overestimate the magnitude of these emissions by about a factor of 2.

These results provide approximate confidence levels that can be placed on these emissions estimates.

3. Past inventories for the Houston area underestimated emissions of alkenes (ethene and propene) from petrochemical facilities by factors between 10 and 100. This experience shows that field experiments combined with modeling can be effective in identification and reconciliation of serious discrepancies in emission inventories.

4. Inverse modeling indicated that the 1990 NEI overestimated $NH_3$ emissions by 25 to 30 percent, and a strong seasonal cycle should be specified for those emissions. Inventory development and improved inverse modeling have reconciled these discrepancies in the 2001 NEI.

The methods illustrated here are important as consistency checks on emission estimates, and provide approximate confidence levels for these estimates. However, it is important to note that these top-down tests cannot be taken necessarily as definitive. With a combination of top-down tests and bottom-up estimates of emissions, disparities between the two require the data analyst and inventory developer to work together. Through cooperative efforts, the differences can be reconciled. The resulting analysis may reveal that bottom-up inventory needs improvement, or that the top-down process has problems, which require resolution. The

ultimate goal is to achieve sufficient accuracy to allow the intended use of the inventory.

The emerging lesson from these evaluations is that without the support of direct measurements, current bottom-up inventories are not yet accurate enough for some technical uses. Yet, bottom-up inventories are indispensable components of photochemical models, and the foundation upon which knowledge of pollutants in the atmosphere is based. The Emission Inventory Flow Diagram (Figure 2.1) shows a proposed solution to this conundrum. It illustrates a continuing process of inventory development, testing through top-down evaluations and reviews, and evaluation in turn of the top-down tests. This process is then repeated until the top-down tests of the inventories indicate sufficient accuracy for the intended use of the inventory. Such an iterative process is required to improve existing inventories, and to develop new ones. The evolving tools discussed in Chapter 6 and the comparison between ambient measurements and emissions estimates exemplified in this chapter are essential for implementing this process.

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CHAPTER 7