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Critical evaluation of US on-road vehicle emission inventories

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Abstract

US Environmental Protection Agency estimates of on-road vehicle emissions are compared with ambient measurements and a fuel-based emission inventory. Several significant weaknesses and strengths are identified. (1) The emission estimates have varied considerably over the past 15 years and are not clearly converging to progressively more accurate and certain results. (2) The most recent emissions estimate accurately captures the rapid decrease in carbon monoxide (CO) and volatile organic compounds (VOC) emissions, but overestimates the magnitude of CO emissions by about a factor of two. (3) The oxides of nitrogen (NO_x) emission estimates for the mid to late 1990s are reasonably accurate, but NO_x emissions have increased through that decade rather than decreased as indicated in emission estimates. (4) The most recent emissions estimate more accurately apportions NO_x emissions between diesel and gasoline fueled vehicles than did earlier reports. (5) The ratio of two specific VOC species that has been characterized by ambient measurements suggests that the inventory speciation of the VOCs is inaccurate by factors of 3–4. These tests lead to the derivation of "inferred emissions" for CO and NO_x from the US on-road vehicle fleet that are consistent with all information used in these tests. Finally, it is shown that the international picture of US emissions has significant inaccuracies and inconsistencies.
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1. Introduction

Emission inventories are essential to our understanding of air quality and climate change issues on local to regional to global scales. The inventories catalog and quantify all needed information regarding emissions of all relevant species to the atmosphere. The relevant species are those that either directly lead to air quality and climate change concerns or are precursors to species of concern that are formed in the atmosphere. Of the species we will address here, the former category includes carbon monoxide (CO) and the latter includes volatile organic compounds (VOCs) and oxides of nitrogen (NO_x), which comprise nitric oxide (NO) and nitrogen dioxide (NO_2). VOCs and NO_x are precursors to the photochemical formation of ozone and particulate matter (PM) throughout the troposphere, particularly intensely in urban areas. Additionally, NO_x is an important contributor to acid deposition. Inventories must accurately specify the quantity of these emitted species, the spatial and temporal pattern of these emissions, and, in the case of VOCs, the chemical speciation of the emissions. The on-road vehicle emissions in the US are the focus of this paper. They include all emissions from gasoline and diesel fueled automobile, truck, and other vehicle traffic on roads and highways. Excluded are all off-road vehicle emissions, such as construction, recreational, farm, and lawn and

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garden vehicles, as well as marine, aircraft, and railway emissions. The goal is to critically evaluate the estimation of the mass of the emitted species, the temporal evolution of the annual average emissions over decadal scales, and the speciation of the VOC emissions.

On-road vehicle emissions are perhaps the most important sector of the US national emission inventory (NEI), but they are difficult to quantify. These emissions are important because (1) they account for a major share of VOC, NO_x, and CO emissions; (2) they provide the majority of the most photochemically reactive anthropogenic VOCs; and (3) these emissions are localized in urban areas, which account for the majority of the National Ambient Air Quality Standard (NAAQS) ozone and PM violations. Accurate estimation of these emissions is difficult since it must integrate the emission factors (e.g. grams emitted per km driven) for a diverse, constantly evolving vehicle fleet multiplied by highly variable activity factors (e.g. average km driven per unit time for each vehicle type under varying vehicle operating conditions such as the frequency of cold starts, high-load accelerations, etc.).

Currently in the US, on-road vehicle emissions are estimated by MOBILE6 (EPA, 2003b), a software application program developed by the US Environmental Protection Agency (US EPA) that provides estimates of emissions from highway motor vehicles. It is the latest in a series of MOBILE models dating back to 1978. MOBILE6 calculates average in-use fleet emission factors for VOCs, NO_x and CO for on-road vehicles for calendar years between 1952 and 2050. The US EPA has made constant efforts to improve emission estimates for on-road vehicles (as well as other categories). In moving from MOBILE5 to MOBILE6, a wealth of data was collected and analyzed to make this adjustment. Additional data are currently being collected to support the development of the next generation on-road vehicle emission model. As a guide for this development, this paper aims to provide tests of the present and previous MOBILE models.

The approach of this paper is to examine the reported on-road vehicle emissions for internal consistency over the past ~25 years, and for inconsistencies with ambient measurements, which may indicate inaccuracies in the inventories. At the outset, it is important to acknowledge that the comparisons with ambient data that we present in this paper are limited in time, space and generality. Consequently, they may not provide definitive conclusions regarding the inventories, but they do identify areas that require additional investigation and refinement.

Wherever possible, NEIs are tested, even though local, county level emission inventories do exist. This approach requires tests based on nationally representative measurement data, rather than simply local measurements; it is taken in order to reach conclusions that are as general 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 has shed light on disparities in the MOBILE6 model (see e.g. Fujita et al., 2003a, b and other papers in the same journal issue).

Below, Section 2 shows that on-road vehicle emissions estimates made over the past 15 years have varied widely; this variation is taken to indicate that there are significant uncertainties in those estimates. Sections 3–5 compare important aspects of estimated emissions with ambient measurements; several discrepancies between inventories and ambient observations are identified. Section 6 derives inferred emissions that resolve the identified discrepancies. Section 7 compares one aspect of the VOC speciation in the inventories to ambient measurements, and concludes that this speciation is also uncertain. Finally, Section 8 summarizes the conclusions, compares them to other work, and discusses implications for international inventories.

2. History of temporal trends of on-road vehicle emissions

The US EPA regularly reports estimated on-road vehicle 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 (EPA, 1990, 1995, 2000, 2003a) 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; more

recent updates have not changed the relevant numbers.) The goal here is to determine if the estimates 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.

Fig. 1 presents estimated on-road vehicle emissions from the six references listed above for VOC, NO_x, and CO. The Trends Reports have been revised annually; both the current year and prior year inventories are updated using the latest models and other information. The 2004 Trends Tables utilize the latest MOBILE6 emission model, and they are consistent with Version 3 of the 1999 US NEI. All the other reports used earlier versions of the MOBILE model to estimate on-road vehicle emissions. In the following discussion, greater emphasis will be placed on the two most recent reports for present and past years. All emissions in Fig. 1 represent the most specific emissions given in the respective reports, but there are the following differences in the defined source categories. Total on-road vehicle emissions are taken from the 1995, 2000 and 2003 Trends Reports and the 2004 Trends Tables. Less detailed breakdown of emissions is given in the earlier reports. Total transport emissions are taken from the 1989 NAPAP and the 1990 Trends Report, except for CO in 1989 NAPAP, where total area sources are taken. These differences are expected to have little effect on the conclusions reached; inclusion of more detailed breakdown in these earlier estimates would generally increase the magnitude of identified discrepancies.

From Fig. 1 it is clear that the different inventory development methods 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% are noted in the VOC and NO_x emissions, respectively, between the 2000 estimate and later estimates. However, the estimate for CO increased by 45%. These comparisons show that emission estimates for recent years differ by at least ~10–15% for VOC and NO_x and ~50% for CO; these differences 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 exceeds all previous estimates by factors of up to 1.35, 1.6 and 2.5 for NO_x, VOC, and CO, respectively. These relatively large factors indicate that less confidence can be placed on the on-road vehicle emission estimates for earlier years of the past two decades.

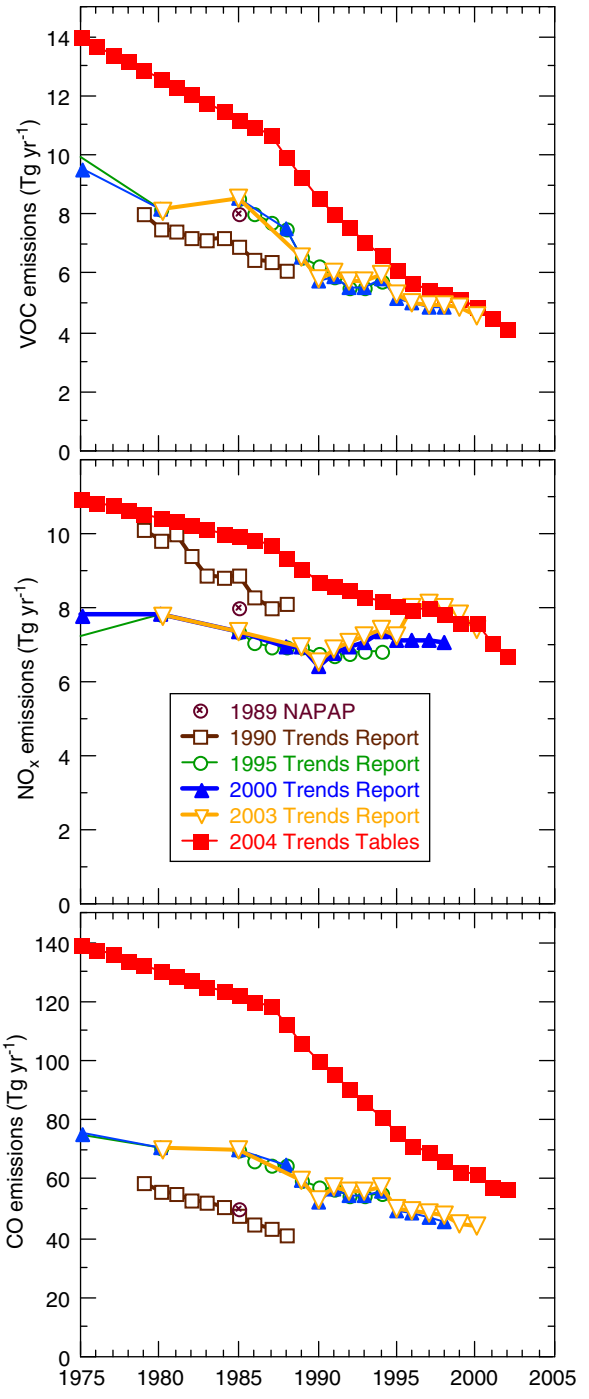

Fig. 1. Temporal trends of national on-road vehicle emissions estimated in the six US inventories discussed in the text.

3. Temporal trend of on-road vehicle CO emissions compared to ambient observations

Analysis of ambient measurements of emitted species can, in many instances, provide insights into the magnitude and temporal trends of the emissions responsible for the ambient concentrations. This section uses the temporal trend of ambient CO concentrations in US urban areas to test the temporal trends of on-road vehicle CO emissions included in inventories. 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 US.

It is possible to select ambient CO data that closely reflect on-road vehicle emissions. Here the maximum CO levels observed in urban areas are utilized. In 2002 (the latest year included in the 2004 Trends Tables), 55% of total CO emissions are attributed to on-road vehicles, which are highly localized in urban areas. The maximum CO levels occur in winter, when there are minimal urban emissions from the two other major CO sources: 22% from off-road vehicles, primarily lawn and garden and recreational vehicles, which maximize in the summer, and 15% from forest and agricultural burning, which also maximize in the summer and generally occur outside urban areas. Background levels of CO transported into urban areas are a minor confounding factor; however, these levels are only a few tenths of a part-per-million by volume (ppmv), so their influence can be neglected. Finally, CO from wood burning in stoves and fireplaces is potentially a significant confounding factor. However, nationally, this source accounts for only 2% of the annual CO emissions, and many urban areas impose wood burning bans during expected high pollution periods, so these emissions are likely to have little influence as well. Hence, temporal trends in maximum urban CO levels can be confidently attributed to trends in CO emissions from on-road vehicles.

Fig. 2 compares the temporal trend of measured CO ambient levels with the emissions from the two most recent emission reports included in Fig. 1. The means of the second highest annual maximum 8-h average observed at more than 300 US urban sites are plotted. These data come from the most recent tabulation (EPA, 2003a), with the exception of the four earliest years, which are taken from an earlier report (EPA, 1998). These earlier years' data represent a smaller number of sites; the tabulated

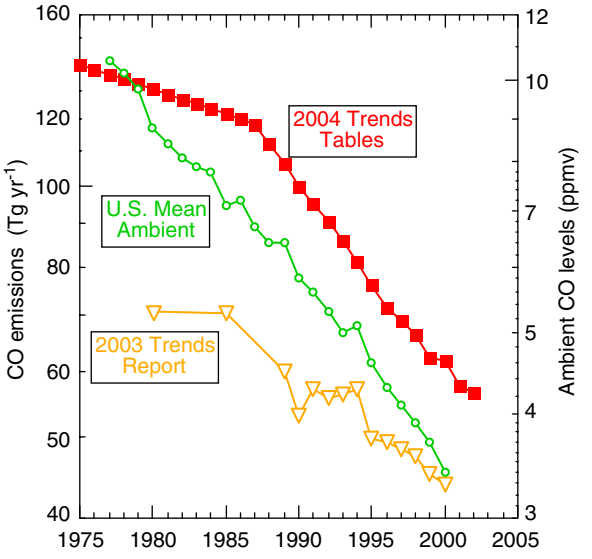

Fig. 2. Semi-log plot of temporal trends of measured urban ambient CO levels compared to estimated national on-road vehicle emissions.

data for these years have been multiplied by 0.97, a factor that normalizes the data between the two reports for six overlapping years. The semi-log plot allows the temporal trends of the curves to be directly compared, since each ordinate spans a factor of four. A quantity that changes at a constant percentage rate (e.g. an exponential decrease) defines a straight line with a slope that reflects the mean annual percent change of the respective quantity.

The temporal trends of the ambient data and of the emissions from the 2004 Trends Tables agree well after 1987. The measured urban ambient levels closely follow ($r^2 = 0.992$ for log transformed data) an exponential decrease with a slope that corresponds to an average decrease of 4.6% year^{-1} from 1977–2000. This yields a factor of three decrease over that 23-year period. The temporal trend of the emissions from the 2004 Trends Tables agrees well (4.9% year^{-1}, $r^2 = 0.995$) from 1987 to 2002, but exhibits a much slower decrease (1.4% year^{-1}, $r^2 = 0.999$) from 1975 to 1987. This comparison indicates that the MOBILE6 model correctly predicts the relative changes in CO emission rates for recent years, but significantly underestimates the decrease before 1987. The average annual decrease of the emissions from the 2003 Trends Report is smaller by about a factor of two (2.5% year^{-1}, $r^2 = 0.91$) for the years shown in Fig. 2. The

MOBILE5 model used in that report predicts a significantly less accurate temporal emission trend for CO. However, these comparisons are confined to testing temporal trends; they provide no information regarding the absolute accuracy of the emission estimates in any particular year or report.

4. Temporal trends of on-road vehicle CO/NO_x emission ratios in NEI compared to ambient measurements

In favorable situations, ratios of ambient concentrations can be directly compared with ratios of the 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 provide an accurate indication of the emission ratios of these species from on-road vehicles in the California South Coast air basin. Here ambient CO/NO_x ratios measured throughout the US are used to test reported CO and NO_x emissions from on-road 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 on-road vehicle emissions. For the CO/NO_x ratio, the separation of the influence of on-road 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, on-road vehicles account for a smaller fraction (35%) of the total NO_x emissions, while the two other major sources (off-road vehicles and industrial processes plus electrical power generation) account for larger fractions (19% and 44%, respectively). It is important to minimize the confounding influence of these two sources. A four-pronged approach is adopted:

1. Only urban areas, where the on-road emissions are localized, are considered. 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 on-road vehicle fleet rather than any particular traffic flow.
3. Data are considered only from the morning, on-road vehicle traffic peak, which minimizes several potential problems. First, this is the time of maximum on-road traffic volume and especially maximum ambient concentrations from those emissions, since they are confined to a shallow boundary layer. Second, this is also likely to be a period of minimum off-road vehicle activity. Third, the influence of industrial and electrical power generation emissions are minimized, because they are predominately released from elevated stacks that inject them above the boundary 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 off-road vehicle contributions to CO and NO_x emissions are also poorly correlated, since lawn and garden gasoline engines dominate CO emissions and off-road diesel engines dominate NO_x emissions; thus, these emissions also have little influence on the slope.

Fig. 3 compares the CO/NO_x ratios derived from the ambient data sets summarized in Table 1 to the CO to NO_x emission ratios from on-road vehicle sources in the two most recent Trends Reports. 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 Fig. 3) are from single sites selected to sample well-mixed urban on-road vehicle emissions. CO and NO_x at these sites are highly correlated ($r^2 \geqslant 0.9$), indicating that the site selection was successful. The Atlanta, GA site has only a short data record (the point in Fig. 3 represents the average for 1999–2001 August data) with weaker correlations ($r^2 = 0.5-0.8$), which reflect the site's closer proximity to local traffic. The Los Angeles data set combines all August data from eight sites

distributed throughout the Los Angeles Basin in southern California. 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 ($r^2 = 0.8-0.9$), which indicates a homogenous on-road vehicle emission mix throughout this region. Finally, the AIRS data set includes all co-located CO and NO_x measurements in the US 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 between CO and NO_x measurements at all of those sites from July and August for 6:00–9:00 a.m. local time. Not surprisingly, these data have weaker correlations ($r^2 = 0.4-0.6$), reflecting not only the proximity of some sites to local traffic sources, but also regional differences in the average on-road vehicle CO to NO_x emission ratio.

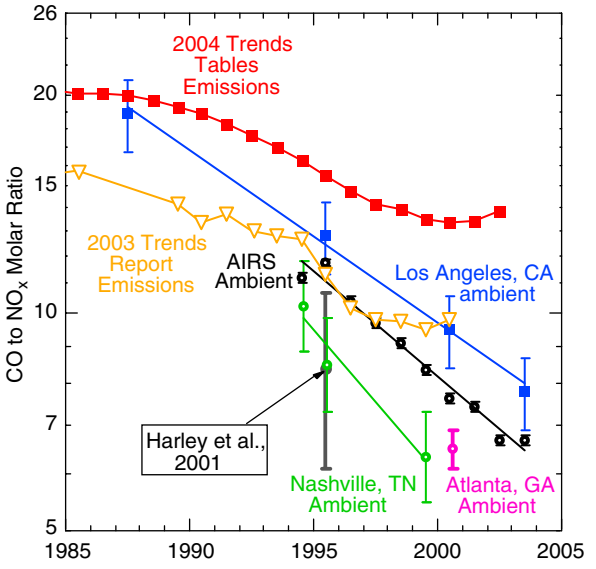

Fig. 3. Semi-log plot of temporal trends of observed urban ambient CO to NO_x ratios compared to ratios from on-road vehicle emission estimates.

There are potential biases in the CO to NO_x emission ratios presented here since they are limited to the morning, on-road vehicle traffic peak, and under these conditions may not be representative of the total vehicle emission inventory. Diesel truck traffic and accompanying NO_x emissions are possibly under-represented due to disproportionate inter-city driving for trucks versus automobiles, which would bias the urban CO/NO_x ratio high compared to the national vehicle emission inventory. Second, the diurnal distributions of gasoline and diesel emissions differ, which again may bias the urban CO/NO_x ratio high since trucks are under-represented in the morning, on-road vehicle traffic peak. Harley et al. (2005) discuss the temporal trends in vehicle emissions in more detail. Our approach here is to focus primarily on the temporal trend of the CO/NO_x ratio and only secondarily on the absolute magnitude. Even if the ratios are significantly biased in absolute value, it is expected that their temporal trend is still accurate because the possible biases are not likely to change strongly on the decadal time scales considered. Further, the agreement shown in the next section between the CO/NO_x ratio derived from ambient measurements and that derived from the fuel-based inventory suggests that the potential biases are not large.

Table 1
CO/NO_x molar emission ratios during morning traffic peaks derived from ambient measurements

Location	Measurement period	Ratio in 2000[a]	Temporal trend[a] (% year^{-1})	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]
US urban	1994–2003	7.9±0.1	−6.6±0.3	0.97	AIRS[d]

[a]Values derived from exponential fits as shown in Fig. 3.
[b]1995 and later data from CARB web site (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 extracted from the EPA AIRS database.

Table 1 and Fig. 3 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 faster decrease in the southeastern US. These patterns could each be compared to the available emission inventory for the respective area but these differences are not great, and only the comparison to the NEI is shown. From this point on, the AIRS trend, which is derived from stations across the entire country and is representative of the other ambient temporal trends, will be taken as representative of national on-road emissions.

Comparison of the ambient data trends with the inventory trends in Fig. 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 ratios also rise above the AIRS 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. For the 2004 Trends Tables, these are not small differences; by 2002, they are greater than a factor of two. Second, the ambient ratios decrease more rapidly than the temporal trend of the inventory 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. Taken together, these two findings indicate that NO_x emission estimates are decreasing too rapidly (or increasing too slowly) to be consistent with the ambient determinations.

The above conclusions require a caveat; the error bars shown in Fig. 3 represent the uncertainty in deriving the temporal slope of the CO/NO_x correlation, but do not include any additional uncertainty due to the possibly confounding effects discussed above. It is not possible to assign reliable confidence limits to the ambient determinations of the on-road vehicle emission ratio, since the magnitude of the confounding effects have not been quantified.

5. Comparison of fuel-based and mileage-based on-road vehicle emissions estimates

A fuel-based approach to emission inventory development provides an effective comparison for the mileage-based method used by the US 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 US locations. The goal here is to use this comparison to test the accuracy of the magnitude of inventory emissions from on-road vehicles.

In Fig. 3, the CO/NO_x emission ratio from the fuel-based inventory (Harley et al., 2001) for Nashville is compared to the ambient ratio discussed in the previous section for that city in the same year. The excellent agreement (although fortuitously good, given the indicated confidence limits) 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.

Fig. 4 compares the results of the fuel-based inventory with the EPA inventory for the same region and time period. The 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 Fig. 4 is a test of these Trends Report emissions, but not the 2004 Trends Tables, which are based on MOBILE6. This comparison leads to three conclusions:

1. There is excellent agreement in the total VOC and NO_x emissions. This comparison increases our confidence in the Trends Reports' estimates of these emissions for 1995.
2. The EPA CO emission estimate is about 40% higher than the fuel-based estimate. This suggests that the inventory overestimate of the CO to NO_x emission ratio discussed in Section 4 is due to an overestimate of the CO emissions rather than an underestimate in the NO_x emissions.
3. Even though the total NO_x emissions agree well, the fraction the EPA MOBILE5-based inventory attributed to diesel-powered vehicles was much smaller (25%) than found in the fuel-based inventory (47%). Fig. 5 shows that the MOBILE6-based 2004 Trends Tables provide

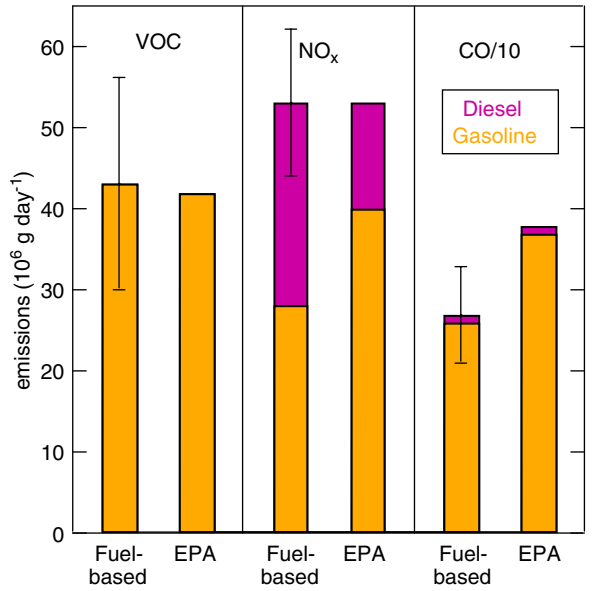

Fig. 4. Comparison of fuel-based emission inventory for Nashville in summer 1995 with the corresponding EPA emission inventory for that county (Harley et al., 2001). The error bars indicate the estimated uncertainty in the fuel-based results. CO emissions are divided by 10 to include on the same ordinate.

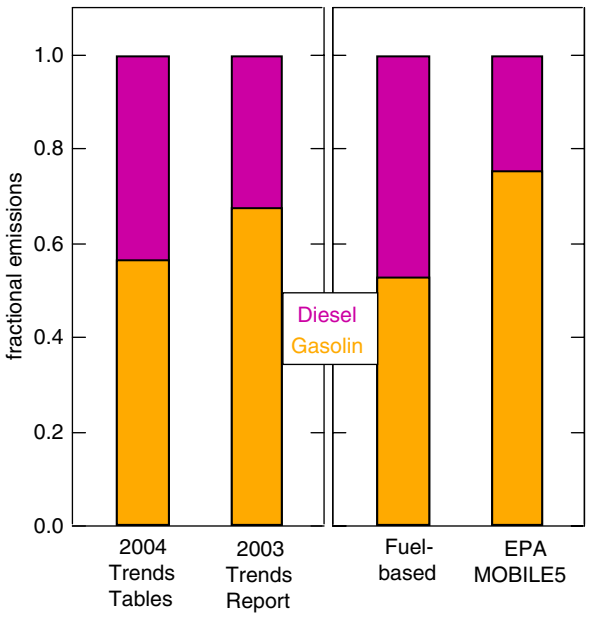

Fig. 5. Comparison of apportionment of NO_x between diesel and gasoline fueled on-road vehicles in two national inventories (left panel) and in the fuel-based and EPA emission inventories for Nashville in summer 1995 from Fig. 4 (right panel).

nationwide emission estimates that are in much closer agreement with the fuel-based inventory.

Both the fuel-based and mileage-based approaches are subject to significant uncertainties. Two particular issues affect the fuel-based approach. First is the uncertainty associated with fuel sales data and apportioning such data to the study area. Second are limitations and errors associated with deriving emission factors from measured on-road vehicle emissions at a relatively small number of sites that may not be representative of the complete driving cycle, and may possibly miss higher CO emissions associated with "cold-starts" of gasoline engines. Examination, testing and modification of both emission inventory approaches until they agree will possibly continue to be a fruitful area of emission inventory development. The experience in California provides a particularly useful example of such development. 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 current California mobile emission model (MVEI 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). Extension of these reconciliation efforts to the NEI and to other regions of the country would be desirable.

6. Reconciliation of estimated on-road 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 in the inventories. Here, emissions, which are consistent with the ambient measurements and the fuel-based inventory, are inferred.

Fig. 6 shows the inferred on-road vehicle emissions for NO_x and CO (black symbols) for the 1990–2000 period. These inferred emissions are derived from four assumptions:

1. Consistent with the fuel-based inventory of Fig. 4, the 1995 NO_x emissions from the 2003 Trends Report are assumed to be accurate, not only in Nashville but nationwide. Thus, the

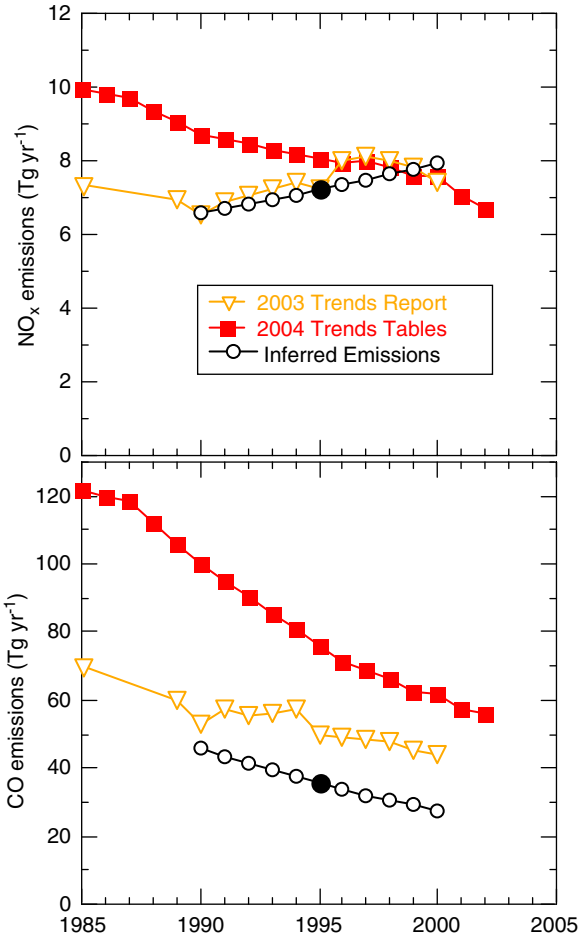

Fig. 6. Temporal trends of national on-road vehicle emissions from the two most recent US inventories in Fig. 1 compared to the emissions inferred from ambient measurements.

inferred NO_x emissions in 1995 are set equal to the value for that year from the 2003 Trends Report (solid black circle in upper panel of Fig. 6).

2. Also consistent with the fuel-based inventory discussion in Section 5, the 1995 CO emissions from the 2003 Trends Report are assumed to be overestimated by 40%, again not only in Nashville but nationwide. Thus, the inferred CO emissions in 1995 are set equal to the value for that year from the 2003 Trends Report divided by 1.4 (solid black circle in lower panel of Fig. 6).
3. Consistent with the discussion in Section 3, CO emissions are assumed to have decreased by 4.9% $year^{-1}$, the rate of decrease of the CO emissions from the 2004 Trends Tables for 1987–2002. Extrapolating this rate of change from 1995 backward and forward in time for 5 years gives the inferred CO emissions for a 10-year period (open black circles in lower panel of Fig. 6).
4. Consistent with the discussion in Section 4, the CO to NO_x emission ratio is assumed to have decreased by 6.6% $year^{-1}$, the rate derived from the nationwide AIRS data set. Combined with the rate of decrease in CO emissions assumed in the preceding paragraph, this implies an increase in NO_x emissions of 1.9% $year^{-1}$. Extrapolating this rate of change backward and forward in time from 1995 gives the inferred NO_x emissions for 10 years (open black circles in upper panel of Fig. 6).

These inferred on-road vehicle emissions differ significantly from the inventory emission estimates. These differences imply significant errors in these estimates, of which two are particularly notable. First, CO emissions in the 2004 Trends Table are overestimated by a factor of two, while the 2003 Trends Report overestimate the emissions by a smaller factor averaging about 40%. Second, the temporal trend of NO_x emissions is poorly defined by the emission inventories. Interestingly, the 2003 Trends Report with an increase averaging 2.8% $year^{-1}$ from 1990 to 1997 closely follows the increasing trend of the inferred NO_x emissions over that period, but this increase is followed by a decrease. In contrast, the 2004 Trends Tables show a continual decrease averaging 1.4% $year^{-1}$ for 1990–2000. Fig. 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% of the inferred NO_x emissions throughout the 10-year period, and the 2004 Trends Table values are within 20% of the inferred NO_x emissions for the years after 1992.

The rate of increase in the inferred on-road vehicle NO_x emissions is derived from the difference between the rates of decrease of two temporal trends (ambient CO levels from Fig. 2 and ambient CO to NO_x ratios from Fig. 3) determined from measurements. Since each of these measurement-derived quantities has some uncertainty, taking the difference between them may be a significant source of uncertainty in the inferred emissions discussed above. The uncertainty involved with taking the CO to NO_x ratios in Fig. 3 as representative of national emissions has not been defined, so it is not

possible to quantify the uncertainty in the temporal trend of the inferred on-road vehicle NO_x emissions.

No substantial inconsistencies have been identified in the total VOC on-road vehicle emissions. The fuel-based and the EPA inventory consistent with the 2003 Trends Report agreed very well for 1995 in Nashville (Fig. 4). The 2004 Trends Tables estimates for years after 1993 are no more than 11% higher than the 2003 Trends Report (Fig. 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% $year^{-1}$, which is in reasonable agreement with the decrease in CO emissions of 4.9% $year^{-1}$ discussed above. This agreement between the temporal trends of CO and VOC on-road vehicle emissions is expected from on-road vehicle emission studies (Parrish et al., 2002). CRC (2004) found good agreement of ambient VOC/NO_x ratios with inventories in the 1998–2000 period, which is in accord with the separate analyses presented here for VOC and NO_x.

It may be fruitful to investigate the cause of the difference in the trend in NO_x on-road vehicle emissions between the 2003 and 2004 reports, and to determine if the methods utilized in the 2003 Trends Report are more accurate than those used to derive the later 2004 Trends Tables. Such an investigation should examine the inconsistency in the apportionment of NO_x emissions between gasoline and diesel fueled vehicles, shown in Fig. 5. The emission factors for diesel vehicles have been stable, while diesel fuel consumption has been increasing. Hence, an underestimate of increasing NO_x emissions from diesel vehicles may underlie this discrepancy.

7. Evaluation of VOC speciation

Evaluation of ambient VOC measurements can provide critical tests of VOC speciation in the NEI. Benzene and acetylene are examined here. Both of these hydrocarbons are in the top 10 in terms of ambient concentrations, and react slowly in the atmosphere. Fortin et al. (2005) argue that these species are primarily emitted by on-road vehicles, and show that the benzene to acetylene ratio is remarkably invariant throughout the country in any given year and exhibits long-term trends in response to VOC emission control measures (Fig. 7). Before 1994, the ratio increased slowly due to the preferential removal of acetylene by automotive catalytic converters. In 1994, in response to the 1990 Clean Air Act Amendments, specific benzene control measures were begun, which dramatically reduced the benzene to acetylene ratio in the following decade.

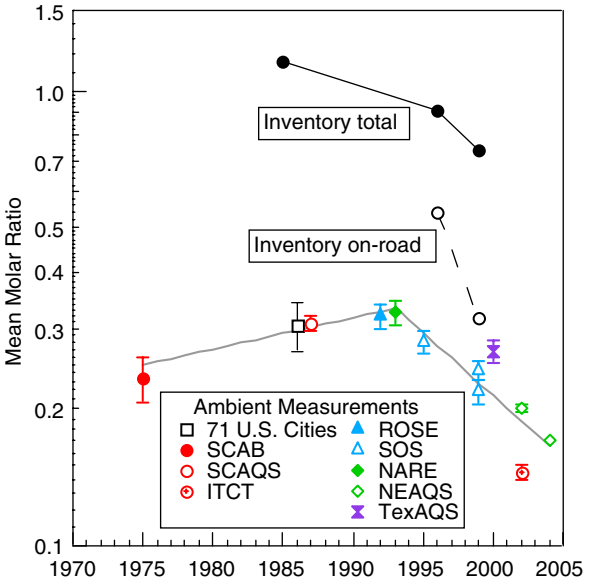

Fig. 7. Semi-log plot of temporal trends of observed ambient benzene to acetylene ratio from field study data compared to inventory ratios. The colors of the symbols indicate geographic location: US Urban (black), California (red), southeast US (blue), northeast US (green), and Texas (purple). The error bars indicate the 95% confidence limit of the mean. The gray lines indicate estimated ambient trends before and after 1993. The inventory ratios are from Table 1. Adapted from Fig. 2 of Fortin et al. (2005).

Table 2
Inventories of US emissions[a] of two VOC species

	Species	NAPAP 1985	NEI 1996	NEI 1999
Inventory total	Benzene	10.69	4.08	3.98
	Acetylene	9.24	4.53	5.38
	Ratio	1.16	0.90	0.74
On-road	Benzene	—	0.94	1.00
	Acetylene	—	1.74	3.15
	Ratio	—	0.54	0.32

[a]Units: 10^5 mol h^{-1}.

The measured ambient ratios and their trend can be compared to the VOC speciation in emission inventories. Table 2 gives benzene and acetylene emissions, both for on-road vehicles and inventory totals, from three recent emission inventories. The NEI 1996 and 1999 numbers were obtained by

applying the SPECIATE software (EPA Clearinghouse for inventories and emissions factors: Speciation; http://www.epa.gov/ttn/chief/emch/speciation/index.html) to the respective NEI. The 1996 values agrees to within 10% with the 1996 National Toxic Air Pollutant inventory for benzene (http://www.epa.gov/ttn/atw/nata/). There are subtle differences in the inventories: the 1985 values are annual average hourly emissions; the 1996 values are hourly average emissions for an ozone season workday; the 1999 values are hourly average emissions for all summer days; and only the 1985 benzene emissions include halobenzenes. These differences are likely small. All fire emissions have been excluded from Table 2, because the ambient measurements were not significantly affected by fire emissions. The corresponding ratios from the three emission inventories are plotted in Fig. 7 in comparison to the ambient data from Fortin et al. (2005) plus an additional datum from the 2004 NEAQS Study [C. Warneke, private communication, 2005].

The comparison between the ambient and inventory ratios in Fig. 7 is quite poor. The inventory ratios for total emissions are a factor of 3–4 higher than the ambient values; those for on-road emissions are also significantly higher than observed. Further, the temporal trends are not clearly in agreement. The ambient measurements must 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 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 reduced benzene emissions, but the inventory benzene emissions (Table 2) have remained approximately constant while the acetylene emissions have increased, particularly in the on-road emissions.

In conclusion, the VOC speciation in the NEI as tested by these two example species are in error by factors of 3–4, and the temporal trend in the inventory emissions is not consistent with the observations. There is a critical need for a re-evaluation of the VOC speciation throughout the NEI. Correctly interpreted, reliable ambient concentration measurements must be one of the important guides for this re-evaluation.

8. Discussion and implications

The previous sections have tested US EPA on-road vehicle emissions estimates through comparisons with ambient measurements and a fuel-based emission inventory. These tests led to the derivation of "inferred emissions" for CO and NO_x from the US on-road vehicle fleet that are consistent with all of the ambient measurements and the fuel-based inventory. Several significant weaknesses and strengths of US EPA estimates of on-road vehicle emissions have been indicated by these tests:

1. Over the past 15 years, the emission estimates have varied considerably (Fig. 1) depending upon the methods used to make the estimates, and it is not clear that the estimates are converging to progressively more accurate and certain results.
2. Maximum ambient CO levels in urban areas (Fig. 2) have decreased by a factor of three from 1977 to 2000. The most recent emissions estimate (2004 Trends Tables) based upon the MOBILE6 model accurately captures this temporal trend for the years since 1987, but earlier emissions estimates underestimated this rate of decrease. However, a fuel-based emission inventory (Fig. 4) and other considerations indicate that the 2004 Trends Tables overestimate the magnitude of the emissions by a factor of ≈ 2.
3. Ambient ratios of CO to NO_x concentrations measured in urban areas (Fig. 3) as well as the fuel-based emission inventory (Fig. 4) indicate that the NO_x emission estimates for the mid to late 1990s are reasonably accurate. However, ambient CO to NO_x ratios have decreased even more rapidly than the CO levels, which indicates that the NO_x emissions have increased through that decade. This increase is in accord with the temporal trend of the NO_x emissions for the early to mid 1990s given in the 2003 Trends Report (Fig. 6) based upon the MOBILE5 model, but not the more recent 2004 Trends Tables. The 2004 Trends Tables more accurately apportions NO_x emissions between diesel and gasoline fueled vehicles than did earlier reports (Fig. 5).
4. The fuel-based emission inventory (Fig. 4) and the close correspondence in the temporal trends of the VOC and CO emissions suggest that the 2004 Trends Tables accurately estimate the magnitude and the temporal trend of VOC emissions. However, the one ratio of specific VOC species that has been characterized by

ambient measurements suggests that the inventory speciation of the VOCs is inaccurate (Fig. 7).

The conclusions reached here can be compared with other works (CRC, 2004; Harley et al., 2005; Richter et al., 2005). With regard to the accuracy of CO emission estimates by the MOBILE6 model, CRC (2004) recently reviewed results from tunnel studies and remote sensing measurements of on-road vehicle emissions that also suggested an overestimate of a factor of ≈ 2 in the MOBILE6 predictions for the CO emissions. However, they also reported measurements of ambient CO/NO_x ratios that 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, their ambient ratio analysis was handicapped by using CO and NO_x data from sensors sited at locations within urban areas that were 3–20 km apart, which precluded use of the correlation analysis employed in Section 4 above. The conclusions from the present work provide a resolution of the contradiction in CRC (2004); the tunnel studies and remote sensing measurements reviewed by CRC (2004) and the analysis of ambient CO/NO_x ratios presented in the present work are all consistent with an overestimate of a factor of ≈ 2 in the MOBILE6 CO emissions.

The increasing temporal trend of on-road vehicle NO_x emissions is perhaps surprising, but is not inconsistent with other recent results. Harley et al. (2005) show that during the 1990s in California, the NO_x emission rate per unit fuel burned in on-road gasoline engines was reduced by a factor of ≈ 2, while the NO_x emission rate from on-road diesel engines remained approximately constant. Over the same period, the on-road fuel use of diesel fuel grew three times faster than gasoline. As a consequence, increased NO_x emissions from diesel engines partly balanced a larger decrease from gasoline vehicles. Overall, the 1990–2000 change in state-wide NO_x emissions from on-road vehicles derived by Harley et al. (2005) corresponds to an annual average decrease of $1.9\%\,year^{-1}$, which is in apparent disagreement with the nation-wide annual average increase of the same magnitude derived in this work. However, California has more aggressive emission controls than the rest of US, so a trend that differs from the rest of the country may be expected. The California data in Fig. 3 and Table 1 support this expectation, since they show the highest and most slowly decreasing ambient CO/NO_x ratios. Richter et al. (2005) present satellite-based observations of the 1996–2004 temporal trends of NO_2 concentrations over populated regions of the globe. While these concentrations have been decreasing in the power plant dominated region of central eastern US, they are increasing over the mobile vehicle dominated urban areas in the mid-west and north-east US. Notably, no significant trend is detectable over the urban areas of California, which further supports the expectation of a differing trend in California.

A comparison of the national US estimates of on-road vehicle emissions to those included in two international inventories, Emission Database for Global Atmospheric Research (EDGAR) and EMEP, allows the accuracy of those emissions to be assessed. The EDGAR inventory (Olivier and Berdowski, 2001) combines information on anthropogenic emission sources and acts in practice as a reference database for many applications. This emission inventory was derived from activity data mostly taken from international statistical data sources and emission factors selected mostly from international publications to ensure a consistent approach across countries. Detailed results have been developed for 1990, 1995 and 2000. The EDGAR inventory shows significant disagreements with the optimum national estimates selected here (the 2004 Trends Tables for VOC and the inferred emissions for NO_x and CO). For 1990, the EDGAR VOC and NO_x estimates are within 11% and 1%, respectively, but the CO estimate is 42% higher. The EDGAR numbers indicate that all three classes of US on-road emissions increased between 1990 and 1995, and then decreased over the following 5 years. This behavior is in contrast with continuing decreases in VOC and CO in the national inventories, and the continuing increase in NO_x emissions derived here. The 2000 EDGAR estimates are in significantly worse agreement with the corresponding optimum national estimates: 38% and 110% higher for VOC and CO, respectively, and 25% lower for NO_x. The EMEP database [UNECE, 2003; available from http://webdab.emep.int/] contains the emission data officially submitted to the UNECE Secretariat by the Parties to the 1979 Long-range Transboundary Air Pollution (LRTAP) Convention. Thus, the US on-road vehicle emissions that have been submitted to EMEP can be no more accurate than the emissions in the NEI discussed in previous sections. However, they also

contain additional significant discrepancies, which evidently have arisen from the inconsistent selection of US EPA emission estimates from MOBILE5 and MOBILE6 model results. It is important that the US review and correct the past submissions to EMEP, and improve the procedures for future submissions.

The analysis in this paper has used ambient data and other considerations to critically evaluate the US national on-road emission inventory. Throughout, it has been assumed that the ambient measurements used in the evaluations are accurate, and that they are correctly interpreted. Any identified inconsistencies therefore imply weaknesses in the inventories, and suggestions for the modification of the inventories were made in order to resolve the discrepancies. However, the accuracy and interpretation of the measurements may have weaknesses themselves. The analysis presented here should be only the first step in a repetitive process of improving both the inventories and their evaluation through such tests as presented here, with the ultimate goal of bringing the inventories and their evaluations into agreement.

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References

CARB, 2002. The 2002 California Almanac of Emissions & Air Quality. California Air Resources Board, Planning and Technical Support Division, Sacramento, CA.

CRC, 2004. Evaluation of the US EPA MOBILE6 highway vehicle emission factor model. Final Report CRC Project E-64, ENVIRON International Corp., Novato, CA.

EPA, 1990. National Air Pollution and Emissions Trends Report, 1988, EPA-450/4-90-002. US Environmental Protection Agency, Washington, DC.

EPA, 1995. National Air Pollutant and Emission Trends Report, 1900–1994, EPA-454/R-95-011. US Environmental Protection Agency, Washington, DC.

EPA, 1998. National Air Quality and Emissions Trends Report, 1996, EPA 454/R-97-013. US Environmental Protection Agency, Washington, DC.

EPA, 2000. National Air Pollutant Emission Trends Report, 1900–1998, EPA-454/R-00-002. US Environmental Protection Agency, Washington, DC.

EPA, 2003a. National Air Quality and Emissions Trends Report, 2003 Special Studies Edition, EPA 454/R-03-005. US Environmental Protection Agency, Washington, DC.

EPA, 2003b. User's Guide to MOBILE6.1 and MOBILE6.2; Mobile Source Emission Factor Model, EPA420-R-03-010. US Environmental Protection Agency, Washington, DC.

Fortin, T.J., Howard, B.J., Parrish, D.D., Goldan, P.D., Kuster, W.C., Atlas, E.L., Harley, R.A., 2005. Temporal changes in U.S. benzene emissions inferred from atmospheric measurements. Environmental Science and Technology 39, 1403–1408. doi:10.1021/es049316n.

Fujita, E.M., et al., 1992. Comparison of emission inventory and ambient concentration ratios of CO, NMOG, and NO_x in California's South Coast air basin. Journal of Air and Waste management Association 42 (3), 264–276.

Fujita, E.M., et al., 2003a. Diurnal and weekday variations in the source contributions of ozone precursors in California's south coast air basin. Journal of Air and Waste management Association 53, 844–863.

Fujita, E.M., Stockwell, W.R., Campbell, D.E., Keislar, R.E., Lawson, D.R., 2003b. Evolution of the magnitude and spatial extent of the weekend ozone effect in California's south coast air basin, 1981–2000. Journal of Air and Waste management Association 53, 802–815.

Harley, R.A., McKeen, S.A., Pearson, J., Rodgers, M.O., Lonneman, W.A., 2001. Analysis of motor vehicle emissions during the Nashville/Middle Tennessee ozone study. Journal of Geophysical Research 106 (D4), 3559–3567.

Harley, R.A., Marr, L.C., Lehner, J.K., Giddings, S.H., 2005. Changes in motor vehicle emissions on diurnal to decadal time scales and effects on atmospheric composition. Environmental Science and Technology 39, 5356–5362.

NARSTO, 2005. Improving emission inventories for effective air quality management across North America: A NARSTO assessment, NARSTO-05-001.

Olivier, J.G.J., Berdowski, A.J.J.M., 2001. Global emissions sources and sinks. In: Berdowski, J., Guicherit, R., Heij, B.J. (Eds.), The Climate System. A.A. Balkema Publishers/Swets & Zeitlinger Publishers, Lisse, The Netherlands, pp. 33–78.

Parrish, D.D., et al., 2002. Decadal change in carbon monoxide to nitrogen oxide ratio in US vehicular emissions. Journal of Geophysical Research 107 (D12), 4140 10.1029/2001J D000720.

Richter, A., Burrows, J.P., Nüß, H., Granier, C., Niemeier, U., 2005. Increase in tropospheric nitrogen dioxide over China observed from space. Nature 437, 129–132.

Saeger, M., et al., 1989. The 1985 NAPAP emissions inventory (version 2): development of the annual data and modelers' tapes, EPA-600/7-89-012a. US Environmental Protection Agency, Washington, DC.

Singer, B.C., Harley, R.A., 2000. A fuel-based inventory of motor vehicle exhaust emissions in the Los Angeles area during summer 1997. Atmospheric Environment 34, 1783–1795.