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Comparison of air pollutant emissions among mega-cities

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ABSTRACT

Ambient measurements of hydrocarbons, carbon monoxide and nitrogen oxides from three mega-cities (Beijing, Mexico City, Tokyo) are compared with similar measurements from US cities in the mid-1980s and the early 2000s. The common hydrocarbon pattern seen in all data sets suggests that emissions associated with gasoline-fueled vehicles dominate in all of these cities. This commonality suggests that it will be efficient and, ultimately, cost effective to proceed with vehicular emission controls in most emerging mega-cities, while proceeding with development of more locally appropriate air quality control strategies through emissions inventory development and ambient air monitoring. Over the three decades covered by the US data sets, the hydrocarbon emissions decreased by a significant factor (something like an order of magnitude), which is greater than suggested by emission inventories, particularly the EDGAR international inventory. The ambient hydrocarbon and CO concentrations reported for the three non-US mega-cities are higher than present US ambient concentrations, but lower than those observed in the 1980s in the US. The one exception to the preceding statement is the high concentrations of CO observed in Beijing, which apparently have a large regional contribution.

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1. Introduction

(Note: Much of this material appeared earlier in a slightly different form as an article in the *IGACtivities Newsletter*, *38*, 22–29 in April 2008.)

The world's mega-cities represent a wide diversity of cultures and histories, with examples of mega-cities on all five major continents. This diversity might be expected to lead to very different patterns of air pollutant emissions. However, as mega-cities develop economically, a convergence of cultures occurs in the sense that automobile fleets and industrial processes develop in similar modes across all cultures. Our goal in this article is to compare and contrast air pollutant emissions in several mega-cities as reflected in measured ambient concentrations of those pollutants with the goal of inferring the degree of similarity of emission sources among these cities.

Our focus here is on major precursors of photochemical smog: non-methane hydrocarbons (NMHC), carbon monoxide (CO), and oxides of nitrogen ($NO + NO_2 = NO_x$). These are the primary pollutants whose emissions fuel the photochemical formation of ozone, other oxidants, and a fraction of the particulate matter (nitrates and secondary organic aerosol) that accumulate in urban atmospheres. We will not address the emissions of sulfur dioxide and primary emissions of particulate matter, which lead to a major fraction of the visibility-reducing aerosol loading in many urban areas. Neither will we address emissions of oxygenated volatile organic species, nor a variety of airborne toxic species, such as mercury and persistent organic pollutants. As a consequence, possible important differences in the emissions of these species between mega-cities will remain unaddressed.

Measurements of ambient concentrations in US cities have revealed marked similarities in the NMHC concentration patterns throughout the country (e.g., Parrish et al., 1998; de Gouw et al., 2005; Warneke et al., 2007; Baker et al., 2008). With the exception of the smaller alkanes, many of the patterns are so constant that deviations from those patterns may indicate measurement problems, rather than actual differences in the ambient concentrations

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(Parrish et al., 1998). Significant deviations from the common pattern can be substantiated only in cities (e.g. Houston) with large industrial sources characteristic of that particular urban area (e.g., Jobson et al., 2004).

One goal of this paper is to compare patterns in the ambient NMHC concentrations in three of the world's mega-cities with those documented in the US. Comprehensive suites of atmospheric measurements in mega-cities have only recently become available. The comparisons here will focus on different cities – Beijing, Mexico City, Tokyo and US cities – and on temporal contrasts – US emissions at present versus in the 1980s.

It should be noted that the discussion presented here is best characterized as suggestive rather than definitive. The available data sets are still quite limited, with the measurements conducted at only one or two sites within a large urban area and for short (about 1 month) time periods. There are differences in the measurement techniques, the seasons and times of day of the measurements, and in the statistical approaches to analyzing the resulting data sets. Nevertheless, the comparisons presented here provide intriguing preliminary findings that provide directions for further study.

2. Data sets

The data sets considered here in detail were collected downwind of Boston and New York City in 2004, in Tokyo in 2003 and 2004, in Beijing in 2005 and in Mexico City during 2006. These data are compared with results of measurements reported in the literature for US cities in the 1980s and the 2000s.

The Tokyo NMHC data were collected during four different Integrated Measurement Program for Aerosol and Oxidant Chemistry in Tokyo (IMPACT) campaigns in the summer and autumn of 2003 and the winter and summer of 2004. The measurements were made at the Komaba campus of the Research Center for Advanced Science and Technology of the University of Tokyo located in the heart of downtown Tokyo. Shirai et al. (2007) and Kondo (2008) provide more information on the IMPACT campaign.

The Beijing measurements were made during August 2005 from the roof of a 6-floor academic building on the campus of Peking University (PKU), located in the northwestern urban area of Beijing. More details of the measurements are available in Song et al. (2007).

The Mexico City measurements were made during the Megacity Initiative: Local and Global Research Observations (MILAGRO) campaign at the T1 site, a suburban location at the Universidad Tecnológica de Tecámac to the northeast of Mexico City during March 2006. The website http://www.eol.ucar.edu/projects/milagro/media/MILAGRO-Factsheet-Final.pdf provides more information on the MILAGRO campaign, as does an article by Molina et al. (2008). A major focus of MILAGRO was characterization of vehicle emissions throughout the urban area. The NMHC data from T1 site are described in detail elsewhere (de Gouw et al., 2008; Welsh-Bon et al., in preparation).

Data from the United States are presented for comparison with these other mega-city data. A survey of NMHC concentrations in 71 US cities was made by the US Environmental Protection Agency in 1984–1988. Seila et al. (1989) presented a summary of the data from the first 39 cities surveyed, and W. A. Lonneman has provided us with the complete data set for comparison purposes. Here these results will be compared with a more recent, similar survey of 28 US cities conducted between 1999 and 2005 (Baker et al., 2008). A detailed NMHC speciation study conducted on a ship immediately downwind of the Boston and New York City urban areas (Warneke et al., 2007) will also be examined. In their work, Warneke et al. (2007) show that their NMHC speciation characterization is generally consistent with that of Baker et al. (2008). All of these US data sets were collected in the summertime. Although most of the US cities investigated cannot be considered mega-cities, the data patterns that are discussed are representative of New York City and Los Angeles, the two US mega-cities.

3. Hydrocarbon emissions

The ambient concentrations of hydrocarbons in the atmosphere of an urban area provide detailed information regarding the emission sources of these species in that area. Section 3.1 examines the relationships between the ambient concentrations of different hydrocarbons and the emission patterns that lead to these relationships. Section 3.2 explores the emission changes over the past three to four decades implied by the limited historical record of hydrocarbon measurements in the US and compares recent US concentrations with current concentrations in the other mega-cities.

3.1. Relative emission patterns of hydrocarbons

Here we examine the patterns of the ambient concentrations of a few selected hydrocarbons (Table 1) across the data sets discussed above. These example species were selected based on several criteria. First, they are among those observed at higher concentrations, which ensures their atmospheric importance and our ability to measure their concentrations accurately and precisely. Second, they are examples from all important hydrocarbon classes found in urban atmospheres: alkanes (n-hexane), alkenes (ethene, or more commonly, ethylene), aromatics (benzene and toluene), and the one important alkyne (ethyne, or more commonly, acetylene). Third, they are all believed to be emitted predominately from anthropogenic rather than biogenic sources. Finally, they represent species emitted from all of the recognized important urban anthropogenic sources. Table 1 lists these urban sources of NMHC and indicates which of the example NMHC are released in substantial quantities from each.

Figs. 1–3 illustrate the relationships between three pairs of the selected NMHC. In each case both members of the pair have similar atmospheric lifetimes with respect to photochemical oxidation by the hydroxyl radical. This oxidation is the primary loss process for NMHC from the atmosphere. Similar lifetimes for a pair of hydrocarbons implies that the ratio of their measured ambient concentrations does not depart from the molar emission ratio of the hydrocarbons, even after photochemical processing of polluted air masses.

In general, Figs. 1–3 show approximately constant ratios of the measured NMHC concentrations, even while the observed concentrations vary widely. The 71 US cities data set, which was collected more than two decades ago, generally shows larger scatter than the other four data sets. This scatter indicates either a greater diversity of sources in the 71 cities surveyed, or perhaps poorer measurement precision because the measurement technology was not nearly as mature at the time of that study. A representative average concentration ratio can be derived from a particular data set in several ways. Here two methods were employed: either the slope was derived from a linear, least-square fit to the observations (with the y-intercept either set to zero or optimized by the least-squares procedure), or the geometric mean ratio was calculated from all pairs of NMHC measurements in the data set. To obtain the "best" ratio estimate the former method was used when the linear correlation coefficient between the two NMHC was ≥ 0.8 and the latter method was used for more poorly correlated data. Specific details of the procedure used for each NMHC pair are given in the figure captions. In each case the "best" average molar ratio is taken to represent the average molar

Table 1
Important sources of NMHC in urban areas, with the primary sources of the example NMHC indicated (after Friedrich and Obermeier, 1999).

Emission Source	n-hexane	ethylene	benzene	toluene	acetylene
Internal Combustion Engines, Gasoline Usage	✓	✓	✓	✓	✓
Fossil Fuel Production, Storage, and Distribution	✓		✓	✓	
Solvent Use	✓			✓	
Industrial Processes		✓	✓	✓	✓
Wood and Biofuel Combustion		✓	✓	✓	✓

emission ratio of those NMHC in the region in which the measurements were made.

The uncertainties of the average molar emission ratios derived in Figs. 1–3 have contributions from the statistical imprecision of the ratio determination and from systematic inaccuracies in the measurement techniques. The statistical imprecision is in all cases small enough to support the number of significant figures given for the derived ratios, i.e. $\leq$10%. However, we have no means to evaluate unknown systematic uncertainties that arise from calibration uncertainties, instrumental differences between studies, etc. This must be considered in the following discussion of apparent molar emission ratio differences between cities.

Fig. 1 presents the analysis of the molar emission ratio of benzene to acetylene derived from five studies. A great deal of similarity between the 71 US cities study and the three non-US mega-cities is clear. The ratios of those four (of the five) data sets are all within 0.29–0.31. Benzene is a pollutant of particular regulatory concern, since it is a demonstrated carcinogen. Fortin et al. (2005) have shown that in the US the benzene to acetylene ratio has decreased since the early 1990s due to policies implemented following the 1990 US Clean Air Act Amendments. These policies included focused efforts to control a selected list of hazardous air pollutants including benzene. The emission ratios shown in Fig. 1 for the two US data sets (0.30 and 0.17) are consistent with this temporal trend. To our knowledge, this change in the benzene to acetylene emission ratio is the only well-documented, systematic temporal change in average US NMHC emission patterns. The three non-US mega-cities exhibit emission ratios very close to the 1990s US emission ratio, before the focus on reducing benzene in US emissions.

Figs. 2 and 3 show the derived molar emission ratios of ethylene to toluene and n-hexane to toluene, respectively. Again, significant similarities between the US cities and the three non-US mega-cities are evident in both figures. The two US studies indicate that the emission ratios have remained near 2 for ethylene to toluene and near 0.45 for n-hexane to toluene over the two decades spanned by the studies. The three mega-cities in all cases have somewhat smaller emission ratios: for ethylene to toluene 25% smaller in Beijing and Mexico City, and about a factor of 2 smaller in Tokyo; for n-hexane to toluene the three mega-city emission ratios are approximately 40–50% smaller than the 2004 US emission ratio.

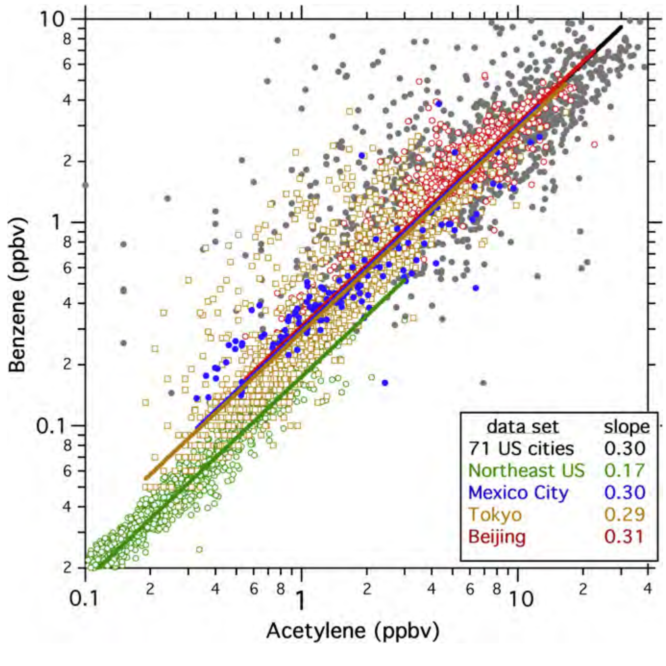

Fig. 1. Relationship between mixing ratios of benzene and acetylene measured in five urban areas. The symbols indicate the individual measurements color-coded as indicated in the figure annotation (except grey for the US cities). The slope of the solid line of the corresponding color indicates the "best" average molar ratio of benzene to acetylene for each data set, and the length of that line indicates the range of the observed acetylene concentrations (except where the length of the US cities line has been truncated for clarity). The numerical values of the slopes are given in the figure annotation. The "best" average ratio was derived from the linear-least-squares fit to the measurements, with the *y*-intercept of the line forced through zero, except for Mexico City and Tokyo, where the "best" average ratio was set equal to the geometric mean ratio of the observations, and the 71 US cities, where the value derived by Fortin et al. (2005) for this data set was taken. The Mexico City benzene data were kindly provided by D. R. Blake.

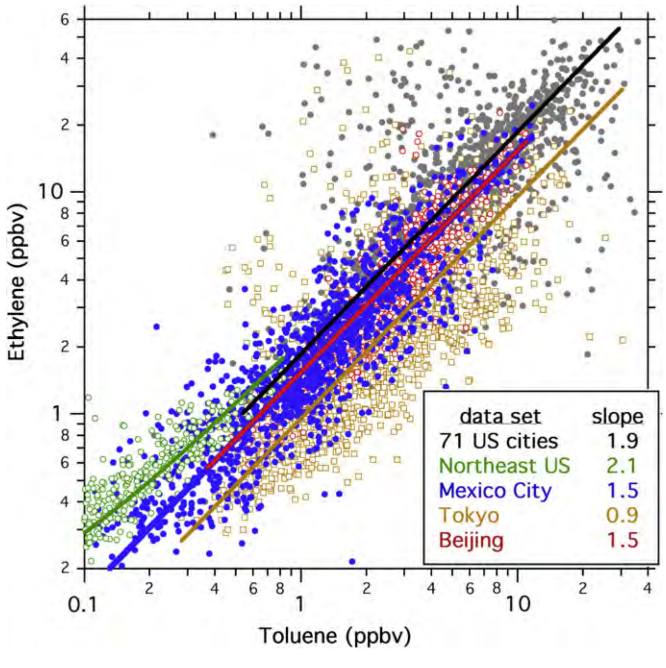

Fig. 2. Relationship between mixing ratios of ethylene and toluene in the same format as Fig. 1. The "best" average molar ratio of ethylene to toluene for Mexico City and Beijing is taken as the slope of the linear-least-squares fit to the measurements, with the *y*-intercept of the line forced through zero. The geometric mean ratio of the observations was taken as the "best" average ratio for the US cities and for Tokyo. The Northeast US ratio was taken as the slope of the linear-least-squares fit to the measurements, with the *y*-intercept allowed to vary; these data were collected aboard a ship, where the lowest concentrations may have been affected by oceanic emissions of ethylene, as reflected by the *y*-intercept of 0.08 ppbv derived from the linear-least-squares fit.

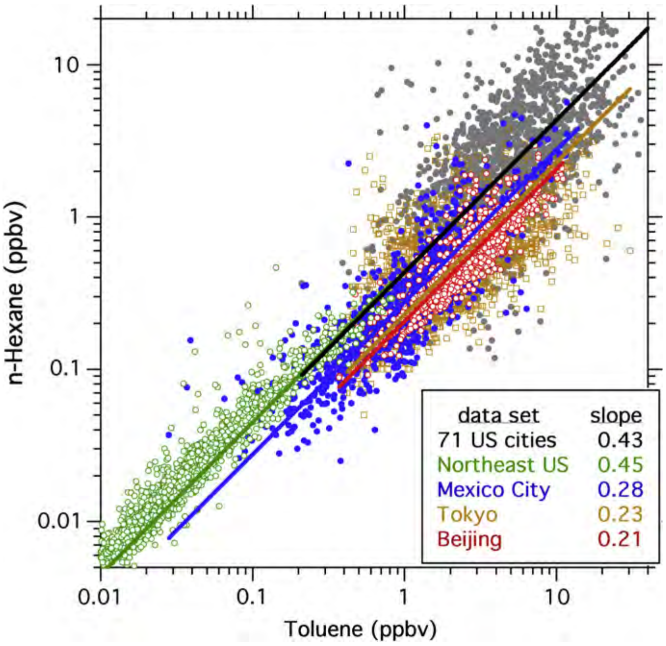

Fig. 3. Relationship between mixing ratios of n-hexane and toluene in the same format as Fig. 1. The "best" average molar ratios of n-hexane to toluene for three data sets are taken as the slope of the linear-least-squares fit to the measurements, with the *y*-intercept of the line forced through zero. The geometric mean ratio of the observations was taken as the "best" average ratio for the 71 US cities data and Tokyo.

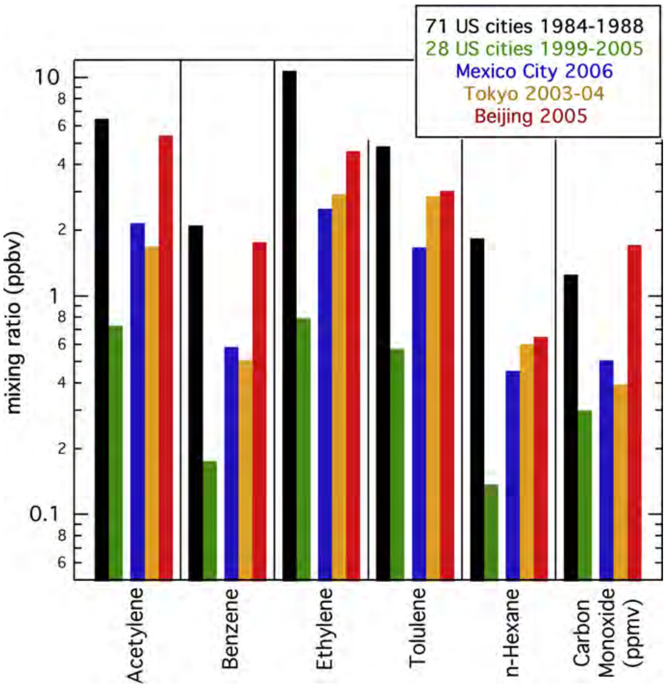

Fig. 4. Mean (except as noted below) mixing ratios of species in five data sets. The median VOC concentrations in US cities in 1984–88 are taken from Table 2 of Seila et al. (1989), and the mean concentrations in US cities in 1999–2005 are the means of the city mean mixing ratios from Table 2 of Baker et al. (2008). Seila et al. (1989) did not report carbon monoxide measurements; the CO concentration for the US cities in 1984–88 is estimated from the median acetylene mixing ratio and the CO to acetylene ratio reported by those same authors for a tunnel study conducted in New York City in 1982 (Lonneman et al., 1986). The Mexico City benzene and CO means were calculated from the data provided by D.R. Blake and L.G Huey, respectively.

Evidently the mega-city emissions are somewhat richer in toluene than are US urban emissions. The importance of industrial and solvent sources of toluene has been identified both in Beijing (Song et al., 2007) and in Tokyo (Shirai et al., 2007). In Fig. 2 the greater scatter in the ethylene–toluene relationship in Tokyo may reflect the varying influence of solvent sources (rich in toluene) and petrochemical sources (rich in ethylene), as suggested by Shirai et al. (2007).

3.2. *Decadal trends of hydrocarbon emissions in the US and comparison with current mega-city emissions*

A striking feature of Figs. 1–3 is that the NMHC concentrations measured in US cities were an order of magnitude or more smaller in 2004 than in the 1980s. This difference is partially due to emission decreases, as well as to the downwind location of the 2004 measurements. Fig. 4 provides a direct comparison of the ambient concentrations of the five example NMHC measured during the two multi-city surveys, one conducted in the mid-1980s and the other in the early 2000s. The reported ambient concentrations of all five NMHC were approximately a factor of 10 lower in the latter study, while the relative amounts of the different NMHC remained quite constant. Importantly, there are significant differences in the sites, measurement protocols, and statistical analysis of the results between these two survey studies. However, these systematic differences are not expected to be large enough to dominate the factor of 10 difference, so we largely attribute the observed differences to a decrease in emissions over the time period between the two studies. Further, the few ambient measurements made during the 1970s (e.g. Mayrsohn et al., 1976) indicate that the NMHC emissions had been significantly higher in the 1970s than in the 1980s. Higher NMHC emissions in the 1970s is supported by a comparison of NMHC measurements made in the Lincoln Tunnel in the New York City area in 1970 and 1982 (Lonneman et al., 1986). The NMHC concentrations were lower by a factor of approximately 4 in the latter study. Thus, ambient measurements and tunnel studies indicate that US NMHC emissions have decreased by a significant factor (something like an order of magnitude) over the past three decades. This decrease has occurred despite large increases in energy use. For example, the US Department of Transportation estimates that the total distance traveled by on-road vehicles in the nation nearly tripled between 1977 and 2007 (http://www.fhwa.dot.gov/policyinformation/travel/tvt/history/). These emission reductions are largely attributed (e.g., Cox et al., 2009) to on-road motor vehicle emission control programs, which include the use of catalytic convertors in exhaust systems, evaporative emission control systems, computerized fuel injection and engine management systems, and reformulated gasoline.

It is notable that an order of magnitude decrease in US NMHC emissions is inconsistent with the US EPA inventory and, particularly, a widely used international emission inventory. A recent US EPA inventory ("1970–2007 Average annual emissions, all criteria pollutants in MS Excel - August 2008" downloaded 21 February 2009 from http://www.epa.gov/ttn/chief/trends/index.html) suggests a decrease in total national volatile organic carbon (VOC) emissions of only a factor of 1.5 between 1975 and 2005. Estimated on-road vehicle emissions, which likely dominate urban NMHC concentrations reported here, decreased by a factor of 3.8, but even this larger decrease is still smaller than what can be consistent with the ambient and tunnel data. Fig. 5 compares US on-road vehicle emissions of VOC, as estimated in the US EPA inventory and by the EDGAR inventory, with exponential trends necessary to account for a factor of 10 or 5 decrease in emissions between 1975 and 2005 (grey lines in Fig. 5). The US EPA inventories are consistent with a decrease no faster than a factor of 5 over three decades, and then only since about 1985. The EDGAR inventory suggests increasing emissions until a maximum was reached in 1995. Clearly, the inconsistencies between the inventoried emissions and those inferred from the measurements, as well as the inconsistencies between the inventories themselves, are of great concern. Retrospective analyses aimed at defining the anthropogenic influences on local, regional and global air quality and tropospheric photochemistry will rely on such reconstructions of emission history. Unless the emission inventory uncertainties can be substantially reduced, issues such as the efficacy of the US control strategies for photochemical air pollution and the anthropogenic influence on the tropospheric ozone budget will remain very uncertain.

Fig. 4 compares the average magnitudes of the ambient NMHC concentrations in the three mega-cities with those in the US, and Figs. 1–3 also provide comparisons of the individual measurements. In all cases the mega-city concentrations are higher than present ambient concentrations in the US cities as derived from the measurements of Baker et al. (2008), but are lower than the ambient concentrations observed in US cities in the 1980s or the even higher levels of the 1970s. It should be noted that there are quite significant differences between the three mega-cities themselves and between them and the US cities with regard to the measurement programs, as well as to the meteorological conditions that control how emissions result in the observed ambient concentrations. At this point it is premature to analyze how the magnitude of the NMHC emissions compares among the three mega-cities.

4. Carbon monoxide emissions

Carbon monoxide is emitted from internal combustion engines as well as from other inefficient combustion processes including the burning of wood and other biofuel. Hence, CO shares important emission sources with NMHC. Fig. 6 compares the emission ratio of CO to acetylene derived from the five urban data sets. All of the derived average emission ratios agree within ±20%. This agreement is perhaps surprising, since the CO emission contribution from wood and other biofuel combustion is expected to be larger from some of the less-developed mega-cities (Beijing and Mexico City), than from the US cities and Tokyo. This agreement is likely enhanced by similar emission ratios of CO to acetylene (and aromatic NMHC) in internal combustion engine exhaust and biomass burning emissions (see e.g. de Gouw et al., 2004). Fig. 4 shows that Beijing emissions are especially rich in CO compared to NMHC emissions, and Fig. 6 shows that there is a large group of the Beijing data that are elevated in CO compared to the average emission ratio. Figs. 4 and 6 show only very small indications of relatively enhanced CO emissions in Mexico City; in fact the ambient data at the highest concentrations, which predominately determine the slope in Fig. 6, indicate that Mexico City has the lowest CO to acetylene emission ratio of all five data sets. de Gouw et al. (2008) also note the relatively large difference in the CO to acetylene emission ratio between Mexico City and the most recent US measurements.

5. Nitrogen oxide emissions

The concentration ratios of CO to nitrogen oxides illustrated in Fig. 7 show much larger differences between cities than found in the NMHC and CO ratio comparisons. (The comparisons in this section are the most uncertain of any included in this paper, as these measurements are very limited, were made by different investigators using different instrumental techniques, and are more difficult to interpret for reasons discussed further below. Nevertheless, they

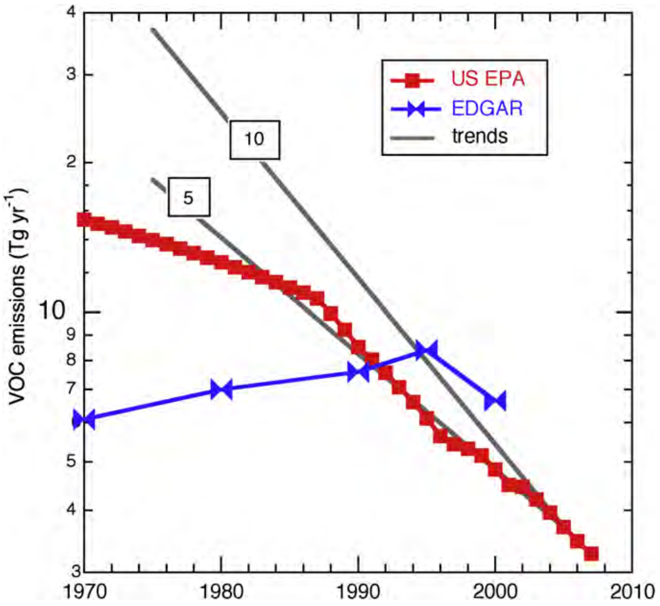

Fig. 5. VOC emissions from on-road vehicles in the US estimated by two emission inventories. The 2008 US EPA emissions are from the latest (August, 2008) emission tables posted on the website of the EPA Technology Transfer Network: Clearinghouse for Inventories & Emission Factors (http://www.epa.gov/ttn/chief/trends/index.html). The EDGAR emissions are from EDGAR 32FT2000 (van Aardenne et al., 2005) for 2000, EDGAR 3.2 (Olivier and Berdowski, 2001) for 1990 and 1995 and EDGAR-HYDE 1.3 (van Aardenne et al., 2001) for 1970, 1980 and 1990. The fossil fuel consumption emissions of EDGAR-HYDE 1.3 were multiplied by 0.864 to bring them into agreement with the 1990 on-road emissions of EDGAR 3.2.

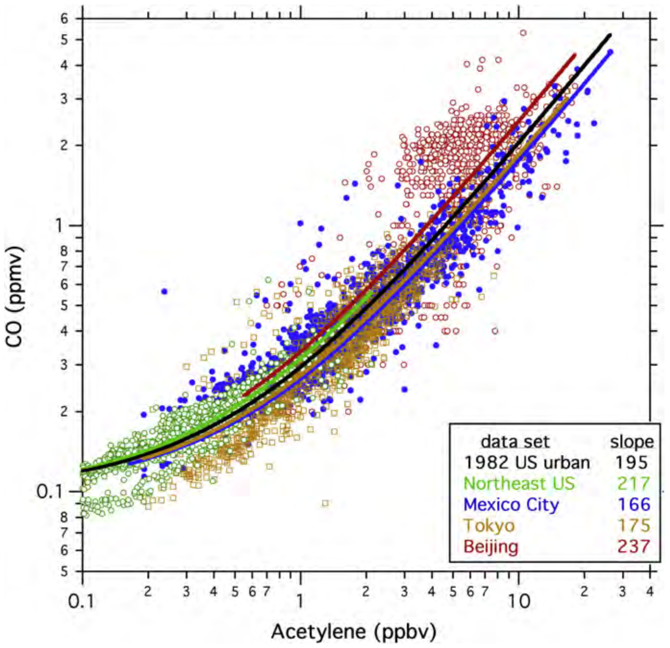

Fig. 6. Relationship between mixing ratios of carbon monoxide and acetylene in the same format as Fig. 1. The "best" average molar ratio of CO to acetylene for each data set is taken as the slope (corrected for the difference in concentration units) of the linear-least-squares fit to the measurements, with the y-intercept of the line forced through 0.1 ppmv. Carbon monoxide measurements were not reported for the 71 US cities study; the slope for the 1982 US urban line is set equal to the CO to acetylene ratio measured in a tunnel study conducted in New York City in 1982 (Lonneman et al., 1986). The Tokyo line is derived as described for Fig. 1. The Mexico City CO data were provided by L.G Huey.

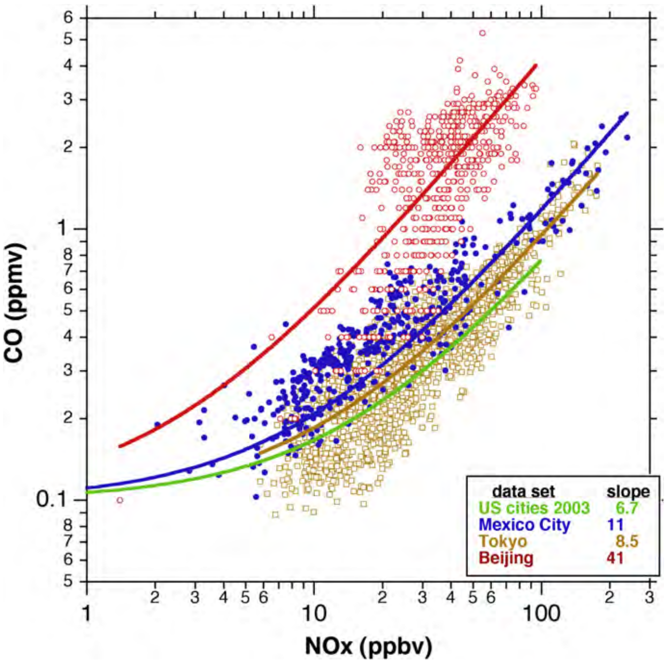

Fig. 7. Relationship between mixing ratios of carbon monoxide and oxides of nitrogen in the same format as Fig. 1. The "best" average molar ratio of CO to NO_x for each data set is taken as the slope (corrected for the difference in concentration units) of the linear-least-squares fit to the measurements, with the *y*-intercept of the line forced through 0.1 ppmv. In Tokyo, Mexico City and Beijing, the measured total reactive oxidized nitrogen (NO_y) measurements are plotted; NO_y is a more nearly conserved measure of the emitted NO_x than are NO_x measurements themselves. The concentration ratio for US cities in 2003 is taken from Fig. 3 of Parrish (2006). For Mexico City, NO data were provided by L.G. Huey and the total higher oxidized nitrogen oxides (the sum of NO_2, organic nitrates and nitric acid) data were provided by R.C. Cohen.

are included as preliminary indications of emission characteristics.) In the US the average urban CO to NO_x concentration ratio has fallen rapidly over the last two decades (see Fig. 3 of Parrish, 2006), reaching 6.7 by 2003 (the value included in Fig. 7), and currently is below 5 in some cities. The CO to NO_x concentration ratio in Beijing in 2005 was a factor of six larger than the 2003 US average. The Mexico City concentration ratio in 2006 was similar to the US emission ratio in the mid-1990s, and the Tokyo ratio in 2003–2004 was similar to the US emission ratio in 1999.

Without careful consideration of the measurement site and measurement time period, it is not possible to directly equate observed urban CO to NO_x concentration ratios to emission ratios. Uncertainties arise from the different lifetimes of CO and NO_x and its oxidation products. CO remains in the atmosphere for periods long enough to be transported over regional to hemispheric scales, while NO_x and even the total reactive oxidized nitrogen (NO_y), is removed on much smaller spatial scales. Thus, local urban concentrations of CO can be affected by upwind sources to a greater extent than the much shorter-lived NO_x or NO_y. This effect appears to influence the Beijing results much more than the other three data sets in Fig. 7. The CO concentrations apparently have a large regional component with concentrations often remaining elevated for a period of several days. This is attributed to regional pollution events, when emissions can build up over the entire, heavily populated east China region under stagnant meteorological conditions. Regional pollution events are not as prevalent in Mexico City, which is relatively isolated from other major population centers, and in the US, where CO emissions have a much stronger local character as evidenced by strong morning peaks in CO concentrations due to the build-up of local pollutant emissions in a shallow, early-morning boundary layer.

The regional sources that apparently influence Beijing likely include biomass burning associated with agricultural practices in the surrounding countryside. This regional source can account for the biomass burning suggested as a common source of CO and acetylene in the previous section. The strong contrast in Fig. 7 of Beijing with the other cities may also reflect the larger contribution of biomass burning, compared to on-road vehicle emissions, in Beijing. Biomass burning emissions are much richer in CO compared to NO_x than are vehicle emissions.

The close agreement of the Mexico City CO to NO_x ratio with that observed in US cities in the mid-1990s can perhaps be taken as an indication that the on-road motor vehicle emission control programs in Mexico City in 2006 performed at about the level of the US program in the mid-1990s. Similarly, the Tokyo program in 2003–2004 was comparable to that in the US at the end of the 1990s. This discussion is speculative, but the important correlated emissions of CO and NO_x are primarily due to on-road vehicle exhaust emissions. An additional variable has a strong influence on the CO to NO_x vehicle emission ratio – the proportion and driving patterns of heavy-duty diesel vehicles. Emissions from these vehicles are relatively rich in NO_x and poor in CO. A complete understanding of the relationships in Fig. 7 would require evaluation of both gasoline and diesel vehicle emissions in each urban area, and an evaluation of the contribution of each vehicle class to the vehicle fleet.

6. Conclusions

The speciation of ambient hydrocarbon concentrations in the mega-cities and other US cities examined here (Figs. 1–4) reveal a large degree of similarity. This similarity spans the cities in North America and Asia, has remained generally constant over the past 2 decades in the US, and persists over wide ranges of absolute concentrations. A two-part hypothesis most likely explains this similarity. First, gasoline-fueled vehicle exhaust and the associated evaporative gasoline emissions dominate the ambient hydrocarbon concentrations in all of these urban areas. Second, there is no large difference in the hydrocarbon composition of gasoline and exhaust emissions between these urban areas.

Comparison of data sets collected in US cities over the past three decades indicates that a substantial decrease (something like an order of magnitude) in hydrocarbon emissions has occurred even while total distance traveled by on-road vehicles has nearly tripled. The ambient concentration data suggest that the emission decrease has been larger than indicated by US emission inventories, and the international EDGAR inventory does not capture any significant decrease. Evidently US strategies aimed toward controlling hydrocarbon emissions, based upon automobile catalytic converters, minimization of gasoline evaporation and other vehicle emission control strategies, have been very successful - indeed more successful than indicated by emission inventories. Unless the emission inventory uncertainties can be substantially reduced, retrospective analyses of anthropogenic influences on tropospheric composition will be uncertain to an important degree.

Emissions inventory development and extensive ambient air monitoring programs have been important and necessary in formulating air quality management programs in the US; however, it is not clear that an effort of similar magnitude need be repeated in each mega-city. Since ambient urban NMHC concentrations are evidently strongly dependent upon vehicle exhaust and gasoline evaporation, it may well be most efficient to simply proceed with vehicular emission controls in most mega-cities before expending the time and expense required for emissions inventory development and ambient air monitoring. Indeed, vehicular emission control measures can likely be expected to yield greater emissions reductions than is generally believed to be the experience in the US, since the success of US controls is underestimated in current inventories. Additionally, of course, in any urban area with significant industrial facilities, such as Tokyo (Shirai et al., 2007) and Houston, Texas (Ryerson et al., 2003), emissions from these sources must be considered in the development of control strategies.

The relationships between emissions discussed in this article and the discussion in the preceding paragraph suggest that the IMPACT measurement program in Tokyo perhaps can provide a model for characterizing emissions in developing mega-cities. This program included measurements of a limited, but carefully selected, set of key NMHC species, plus CO, NO_x and NO_y, during a few measurement periods of limited duration in different seasons. These data sets were successfully analyzed to provide detailed information regarding the important hydrocarbon emission sources in the Tokyo urban area. An approach of continuously measuring a more extensive list of NMHC species at many sites in an urban area would likely provide little additional useful information, and require much greater effort. Given the usual limitation of resources, the IMPACT program provides a possible guide for formulating measurement programs in other urban areas.

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