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Evaluation of vehicle emission inventories for carbon monoxide and nitrogen oxides for Bogotá, Buenos Aires, Santiago, and São Paulo

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ABSTRACT

We use concurrent morning peak observations of carbon monoxide (CO) and nitrogen oxides (NO_x) to evaluate mobile emissions estimates for CO and NO_x at Bogotá (Colombia), Buenos Aires (Argentina), Santiago (Chile) and São Paulo (Brazil). In all cities, molar ratios of CO to NO_x decrease over the last 10–15 years. These ratios are not captured by available inventories. Comparison among inventories suggests that major uncertainties are linked to inadequate emission factors for CO and inadequate activity data for NO_x. These results, in combination with previous studies, suggest that current NO_x emissions are overestimated by a factor of up to 3 in Santiago and São Paulo, and Buenos Aires shows a slight overestimate by 20%. In the case of Bogotá we suspect that the current CO emission inventory is overestimated. Available observations provide valuable information, as exemplified hereby, but more careful attention must be paid to calibration and continuity of the stations.

1. Introduction

In South American megacities, relatively inaccurate emission inventories and simple emission-receptor models have been used to define curbing measures, mostly dealing with industrial sources, and focusing on acute health impacts. As environmental objectives become more ambitious, considering for instance chronic health effects, addressing secondary particles or considering climatic impacts, the need for cost-effective measures requires of more reliable and locally representative emission inventories. According to current inventories, traffic emissions are responsible for 1/3 to 2/3 of the direct emissions of inhalable particles, and for the vast majority of ozone precursors (See references in Section 2). Emission estimates are generally very difficult to make, and this is particularly cumbersome in the case of mobile emissions for which one must consider fuel type and consumption, vehicle technology and the conditions of use for very heterogeneous fleets (e.g., Smit et al., 2010).

In this work, we evaluate emission estimates for mobile emissions of carbon monoxide (CO) and nitrogen oxides (NO_x), including nitric oxide (NO) and nitrogen dioxide (NO_2), in terms of their consistency with observations. We follow the approach by Parrish et al. (2002), i.e., we compare the morning peak concentration ratios of CO and NO_x with the corresponding emission ratios for mobile sources. In this approach it is assumed that morning peak concentrations respond mostly to local emissions because atmospheric mixing is relatively unimportant at these hours. Then, for stations where mobile sources dominate, concentrations should reflect fresh mobile emissions, in particular those of CO and NO_x. A similar approach was previously used by Vivanco and Andrade (2006) to analyze emission estimates for São Paulo. Bogo et al. (2001) and Reich et al. (2006) did analyze CO to NO_x ratios in Buenos Aires but considering all data, not just the morning rush hour.

The next section addresses available mobile emission estimates for Bogotá, Buenos Aires, Santiago and São Paulo, including those obtained for these cities using a simple but standardized methodology, i.e., the International Vehicle Emissions (IVE) model (e.g., Davis et al., 2005). Section three discusses the quality of CO and NO_x data in the cities considered. Data analyses and results are shown in Section 4. Conclusions are presented in Section 5.

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2. Mobile emission estimates for selected South American cities

CO emissions originate from incomplete combustion of fuel, and they are higher for gasoline vehicles than for diesel vehicles (e.g., Heywood, 1988). NO_x emissions are associated to high-temperature and high-oxygen processes, and they occur mainly in the form of NO but in diesel vehicles NO_2 can constitute a significant fraction of NO_x ($\sim$30%) (e.g., Heywood, 1988).

Biofuels are identified as a viable alternative for developing countries as these fuels can be produced domestically reducing petroleum dependence (Liaquat et al., 2010). Brazil adopted in 2003 flex-fuel cars that utilize primarily either anhydrous bio-ethanol/gasoline or a 22% bio-ethanol gasoline blend (CETESB, 2010). Colombia has been using 10% ethanol in gasoline since 2005 and 5% palm oil ethyl ester in diesel since 2008 (Behrentz et al., 2009). Biofuels, both biodiesel and ethanol, have higher oxygen content than petroleum based fuels, which has been shown to result in lower emissions of particles, sulfur, CO, etc. (e.g., Machado Corrêa and Arbilla, 2008). Reductions in NO_x emissions are subject to more debate (e.g., Liaquat et al., 2010).

Compressed natural gas (CNG) is widely used as fuel for light-duty vehicles in Argentina since the mid 90's, adding up to 14% of the fleet (D'Angiola et al., 2010). In Bogotá, 7% of the fleet uses CNG. Santiago and São Paulo show a relatively negligible number of CNG vehicles. Gasoline cars have been converted to use gasoline and CNG, which is not optimal in terms of engine functioning and emissions. D'Angiola et al. (2010) analyzed the impact of the introduction of CNG in Buenos Aires finding, among other things, that it has reduced the emission levels of CO and increased NO_x emissions.

Inspection and maintenance of vehicles in the four cities considered here vary: from Buenos Aires, where there is no inspection at all, Bogotá and São Paulo having limited systems only for CO and HC, to the sophisticated maintenance and inspection applied in Santiago, including measurement of NO_x under load since 2008.

In the case of South American cities simple (e.g., Davis et al., 2005) and complex methodologies (e.g., Corvalán et al., 2002) have been used to estimate mobile emissions. The International Vehicle Emissions (IVE) model (e.g., Davis et al., 2005) has been used in various cities around the world including Bogotá, Buenos Aires, Santiago and São Paulo. This provides a basis for comparison among these cities.

2.1. Bogotá

Zárate et al. (2007) estimated emissions for base year 2002 for particulate matter (PM), CO, NO_x, volatile organic compounds (VOCs), sulfur dioxide (SO_2), methane and carbon dioxide. Giraldo et al. (2006) estimated mobile emissions using the IVE model, including motorcycles. The most recent version of the emission inventory for Bogotá is for base year 2007 (Behrentz et al., 2009). These authors used on-board measurements to infer emission factors for PM, CO, NO_x and VOCs from mobile sources. Rojas et al. (2010) completed this inventory adding diesel vehicles, and disaggregated them in a spatial grid of 1×1 km^2.

The most recent results show that gasoline and CNG personal cars (PCs) and taxis, together with motorcycles emit more than 90% of mobile CO emissions and nearly 60% of mobile NO_x emissions.

2.2. Buenos Aires

A first inventory for Buenos Aires estimated CO, NO_x, VOCs, PM and SO_2 emissions for 1996 (Weaver and Balam, 1999). Mazzeo and Venegas (2003) reported CO and NO_x without specifying the year of the inventory. The most recent and complete emission estimate for mobile sources is the one by D'Angiola et al. (2010). CO emissions are dominated by PCs older than 6 years old without catalytic converters or with systems out of maintenance. NO_x emissions are dominated by the heavy duty vehicles (HDVs) that account with 34% of the emissions, followed by PCs, suburban vehicles and taxis using CNG with 20%, and by gasoline PCs emitting the 13%.

2.3. Santiago

Environmental authorities have supported the formulation of emission inventories for base years 1997, 2000, and 2005, and a projection for 2010 (CENMA, 1997; CENMA, 2000; DICTUC, 2007). Mobile emissions were estimated according to a bottom-up methodology (Corvalán et al., 2002). In general, on-road mobile emissions of CO are dominated by gasoline vehicles (>90%), mainly PCs. NO_x emissions are mainly attributed to gasoline and diesel being the fraction attributed to diesel 53% in the 2010 inventory and 66% in the 2000 inventory for NO_x.

In this study, we use the spatially disaggregated inventory described in Saide et al. (2011). It must be pointed out that even though total emissions are readily available over the Internet, the disaggregated emission inventory is not.

2.4. São Paulo

According to the emission estimates provided by Environmental Agency of the State of São Paulo (CETESB, 2010), between 2001 and 2009, CO emissions have declined by 7%, with the largest reduction occurring in 2005 when there was a correction in the methodology for obtaining the total number of vehicles. The official inventory for the light fleet is calculated based on the measurements of emissions factors in a dynamometer for new vehicles and then multiplied by an aging factor according to the age of the fleet. How many kilometers the light and duty fleets run each day on average is also considered. This inventory is not spatially disaggregated. NO_x emissions also diminished between 2001 and 2009 but only by 3%. The evaluation of the emission inventory for diesel trucks and buses is performed based on data from type of motor, in g/kWh.

In the case of CO, gasoline vehicles stand for roughly half of the total mobile emissions, followed by diesel engines that correspond to ca. 25% of the total CO emissions. Alcohol stands for 13% of the emissions of CO. Over time, there is a growing contribution from motorcycles, from 13% in 2001–18% in 2009. NO_x emissions are dominated by diesel engines that stand for ca. 83% of the total, followed by gasoline engines that contribute with 12% of the total. Alcohol stands for ca. 4% of the total NO_x mobile emissions. The diesel fleet in Brazil is a significant source of particles, and 20% of the fleet is older than 30 years and the light vehicle fleet is on average 10 years old (www.denatran.gov.br). São Paulo has now 630 vehicles for thousand habitants. Between 2000 and 2010, the automobile fleet increased 27%, and the motorcycle fleet increased 136%.

3. CO and NO_x observations

We have used hourly averaged data compiled by the official monitoring networks in Bogotá, Santiago and São Paulo. In the case of Buenos Aires, due to a lack of access to historical data, we complemented one year of official data with data collected at one monitoring site located in front of a highway. These data were subject to various quality control checks. After a careful visual observation of the data series, extreme values were suppressed from the database by excluding the 2 percentile upper and lower tails of the distribution of the logarithm of the values. The time series were also checked with respect to the detection limit of the

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instruments, which is nevertheless usually below the lower 2-percentile cut. To ensure capturing the seasonal and diurnal cycles, we only kept years and stations for which we had 75% of completeness every 8 h for each day and 75% of the data for each season of the year. Diurnal cycles of CO and NO_x mixing ratios were compared to diurnal traffic activity data to identify the morning peak in CO and NO_x that could be attributed to mobile sources. The application of these filtering criteria precluded the use of Bogotá data for a multi-year analysis due to the discontinuity of the data and calibration problems. Similar problems but to a lesser extent were found at all cities. This highlights the need for improvement and more careful quality control in present monitoring networks. A summary of the characteristics of the stations considered in this study is shown in Table 1.

Datasets for Bogotá are partially available to the public on the website of the city's Secretary of the Environment (http://www.secretariadeambiente.gov.cohttp://201.245.192.254:81/). There are six stations where CO and NO_x are concurrently measured. Whereas no seasonal cycle was apparent, a strong diurnal cycle with two CO and NO_x maxima was shown at all the stations. The morning maximum occurs between 7 and 8 AM, responding to the traffic rush hour and it is much sharper than the afternoon maximum, centered at 8 PM, related to both the traffic rush hour and the poorer atmospheric mixing at night.

During the last twenty years, institutions have performed air quality measurements in the Buenos Aires region in an uncoordinated manner, resulting in fragmented and scarce information. For this work, we obtained from city officials one year of CO and NO_x hourly data, for 2009. The corresponding monitoring site, named Centenario and located at the center of the city, is characterized for a dense vehicular traffic. We complemented the official data set with a two month monitoring campaign at a site (CNEA) located in front of a highway located in the border between the city itself and the neighboring districts. The CNEA monitoring site was located at a height of 8 m above the ground. Non-dispersive infrared absorption was used to continuously measure CO with a HORIBA monitor, model APMA-360 using a gas standard of 12.5 ppm to fix the span scale calibration. Chemiluminiscence was used to measure NO_x also in continuous manner, with a HORIBA monitor APNA-360 calibrated with a gas standard of NO of 5.06 and 99.7 ppm diluted with a 1:10 000 ratio by means of a SGGU-514 dilutor device. A marked diurnal cycle is apparent from the observations available at Buenos Aires following vehicle activity (See Fig. 1). While these data do not show a marked seasonal pattern, historical data show higher concentrations from May to October than in the hot summer months.

CO and NO_x have been concurrently measured at three stations in Santiago since 2000 by the regional office of the Ministry of Health. All stations show a marked seasonal cycle with highest concentrations of CO and NO_x in winter. A strong diurnal cycle is also apparent. Cerrillos and Pudahuel stations, located in low income industrial and residential areas to the south-west and west of the basin, show two maxima. A sharp morning maximum around 8 AM and a broad maximum in the late afternoon and evening hours centered at 7 PM. Las Condes, a high-income area to the north-east of the city, shows a primary morning maximum around 9 AM and a secondary maximum in the mid-morning. The evening maximum is broader at Las Condes than in Cerrillos and Pudahuel. These behaviors follow on the one hand, the diurnal cycle of emissions, mainly mobile sources discussed earlier, and on the other hand, from the characteristic radiatively driven air circulation of the Santiago basin, with very stable nights and nearly calm conditions, and south-westerly light winds during the afternoon. The latter partially explains the broader evening peak observed at Las Condes. The mixing conditions result in a very depressed or collapsed boundary layer during nighttime, particularly in winter and a convective layer in the afternoon hours, particularly in summer.

In São Paulo air pollution monitoring started in late 1972 with 14 stations for measurement of black smoke and SO_2 under the responsibility of CETESB. Nowadays 21 automatic stations are in operation in the Metropolitan Area of São Paulo, and 40 automatic and 47 manual in São Paulo state. The highest concentrations of CO and NO_x occur during winter, which is characterized as a dry period, with clear skies, subsidence and thermal inversions. There is also an increase in the concentrations during the night due to increased atmospheric stability.

4. Results

4.1. Bogotá

Although the air quality monitoring network has been active for more than a decade, only the period between 2005 and 2010 was considered to have the appropriate quality to observe the trend in measured CO/NO_x ratio and compare it with that from emission

Table 1
Monitoring stations where concurrent measurements of CO and NO_x are available and whose data were used in this study.

City	Station Name	Latitude (S)	Longitude (W)	Altitude (m.a.s.l.)	Characteristics
Bogotá	Ferias	−4.69	74. 1	2560	Commercial and medium-density residential area with high light- and heavy duty vehicular traffic
	Simón Bolívar	−4.66	74.1	2580	Institutional and commercial area with high light-duty vehicular traffic and public buses
Buenos Aires	Centenario	34.61	58. 44	30	Residential and commercial area close to avenues and streets with heavy traffic of cars and buses and trucks.
	CNEA	34.61	58.52	35	Institutional and commercial area in front to a highway
São Paulo	P. D. Pedro	23.55	46.63	740	In the old downtown city, characterized by traffic of light and heavy (diesel buses)
	Ibirapuera	23.59	46.66	750	A park in a residential area. Main avenues are 250m apart from the station.
	Congonhas	23.61	46.66	760	Commercial area with heavy traffic of light and diesel trucks. Close to the central airport of São Paulo
	Cerqueira Cesar	23.55	46.67	817	In the area of the Faculty of Health Public close to streets with heavy traffic of cars and buses.
	São Caetano do Sul	23.61	46.56	740	Residential and industrial area
	Osasco	23.52	46.79	740	Residential, commercial, and vehicular area
Santiago	Cerrillos	33.49	70.71	516	Low income residential and industrial area
	Pudahuel	33.43	70.75	493	Low income residential area
	Las Condes	33.37	70.52	774	High income residential area

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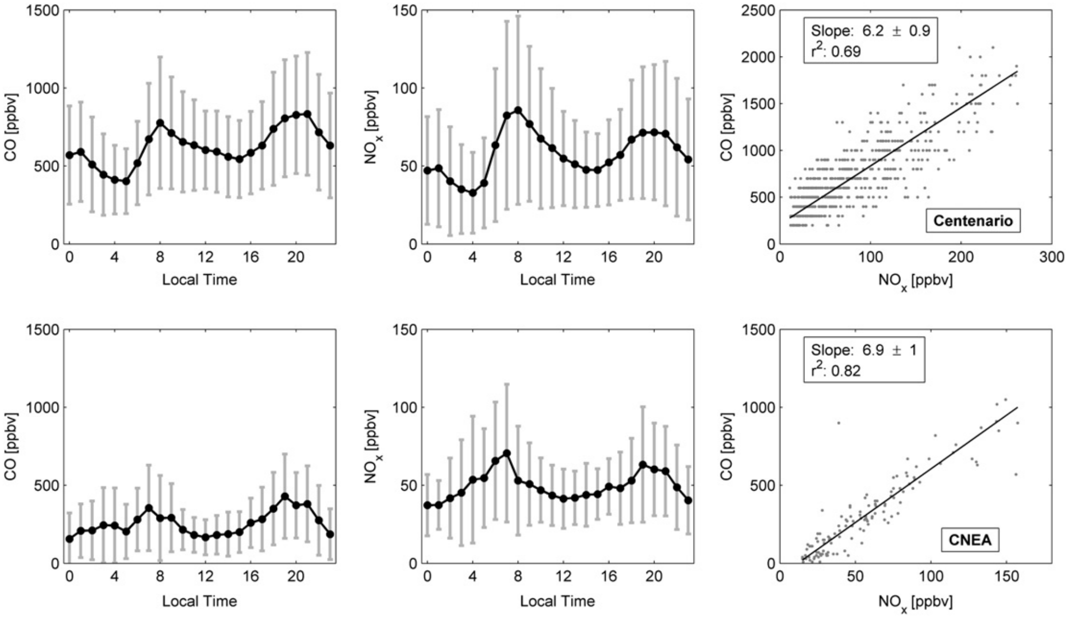

Fig. 1. Observations and CO to NO_x regressions for Buenos Aires data. Upper panel: one year data collected at Centenario in 2009. Lower panel: One month data collected for this work at CNEA in late 2010. Diurnal cycles of CO (left panel) and NO_x (middle panel), and regressions (right panel) weighted with the corresponding CO and NO_x uncertainties. The value of r^2 indicated corresponds to the correlation coefficient for a standard CO vs. NO_x regression.

inventories. Ambient CO/NO_x ratio decreased in both Ferias and Simón Bolívar stations at a similar rate, but its values were consistently and significantly higher in the Ferias station.

Mobile emission inventories estimated for 2005 and 2007 showed CO/NO_x ratios fairly consistent with the observed trend. CO/NO_x values from Giraldo et al. (2006) emission inventory is close to observations at Ferias station, whereas the inventory by Rojas et al. (2010) was closer to Simón Bolívar observations. The consistency in CO/NO_x ratio values between inventories was not kept when evaluating total mobile source CO or NO_x emissions, so no clear trend was observed for either pollutant (not shown). CO and NO_x emissions showed significant differences between inventories developed for the same base years. In the 2005 case, Giraldo et al. (2006) overestimated CO emissions by a factor of almost 3 and NO_x emissions by a factor of more than 3 when compared with Behrentz et al. (2005). For the base year 2008, Rojas et al. (2010) overestimated CO emissions by 52% and NO_x emissions by 92% when compared to Behrentz et al. (2009), although basically the same emission factors were used for PCs. Such difference could be influenced by CO and NO_x emission factors for diesel engines, which were not considered by Behrentz et al. (2009).

The CO/NO_x molar ratio corresponding to the disaggregated emissions for 2008 developed by Rojas et al. (2010) is shown in Fig. 2. Values are roughly between 10 and 20, the highest values being found in the edges of the city and the lowest values, along the intercity roads leaving the city.

4.2. Buenos Aires

Both CNEA and Centenario monitoring stations show similar ambient CO to NO_x molar ratios, i.e., (6.9 ± 1.0) and (6.2 ± 0.9) respectively (See Fig. 1). Bogo et al. (2001) and Reich et al. (2006) obtained a ratio of roughly 14 using measurements from 1999 to 2001 respectively. Three reasons may explain this difference: (1) the increased use of natural gas by the fleet of Buenos Aires, mainly in cars and light-duty vehicles; (2) the monitoring sites of previous studies were located near or in front of streets with a low influence of heavy duty vehicles (trucks and coaches) that usually burn diesel oil and represents the 40% of the total NO_x Buenos Aires Metropolitan Area emissions, whereas the sites considered in this work are closer to the average circulating fleet; and (3), in previous works, authors included all the hours of the day, while here we are including only the morning peak concentration ratios.Measurements at CNEA in 2010 and at Centenario in 2009 are consistent with the inventory ratio for the year 2006, for which a value of (6.6 ± 1.7) was obtained. In Fig. 2 (middle panel) the CO/NO_x molar ratio is presented spatially disaggregated showing a range from 1 to 12 where the lower values correspond to highways with trucks and coaches burning diesel as the main emitters, and higher values in areas where heavy diesel vehicles are absent in the inventory. Obtaining a similar ratio at CNEA and Centenario is a somewhat surprising since CNEA is located by a highway with a larger contribution of diesel vehicles than that of Centenario. This suggests that the categorized activity data requires further refinement.

4.3. Santiago

Ambient CO/NO_x ratios in Santiago decreased exponentially between 2000 and 2010 at all three stations in Santiago (See Fig. 3). The decrease is not well captured by the emission estimates that show a slight increase over the same period. Emission estimates for CO and NO_x suggest an increase of ca. 13% over the same decade. CO mixing ratios have in fact decreased over the decade at all stations (not shown), whereas NO_x observations show no significant trend. This suggests that the change in CO/NO_x ratios is due a decrease in CO emissions from mobile sources. It must be pointed out that in early 2007 a new transportation system (Transantiago) was implemented in Santiago aiming at renewing and reducing the bus fleet. Unfortunately, design and implementation errors made it necessary to re-introduce old buses, and promoted the use of personal cars and motorcycles, possibly leading to an increase of CO emissions. Also, since natural gas supply from Argentina was cut in 2007, industrial sources shifted to oil, leading to increased emissions. All in all, these factors may explain a decline in the rate of change of CO to NO_x ratios after 2007.

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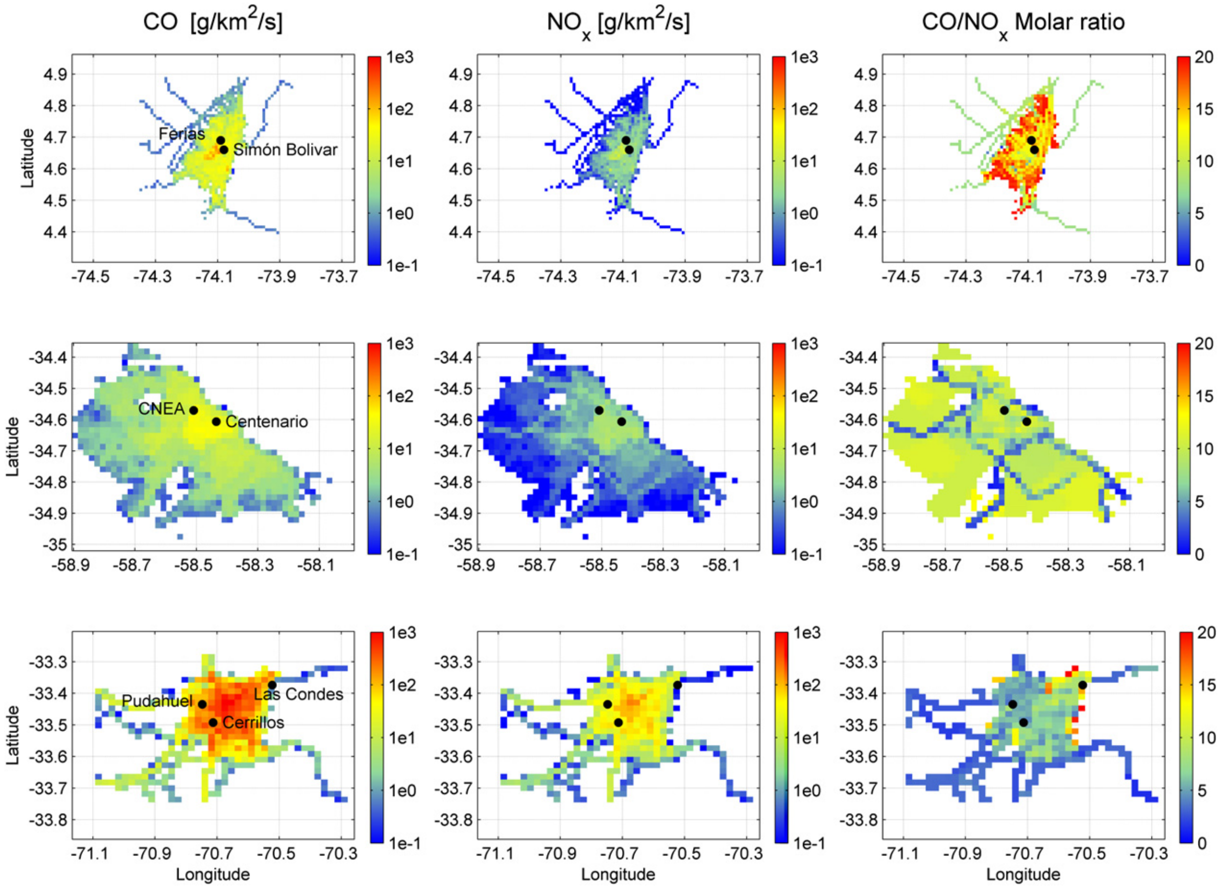

Fig. 2. Disaggregated emissions of CO (in g CO/km^2 s, left panels) and NO_x (in g NO_x/km^2 s, assuming 90% NO and 10% NO_2) middle panels, and the corresponding CO to NO_x molar ratio (right panels), for Bogotá (upper panel), Buenos Aires (middle panel), and Santiago (lower panel). The location of the monitoring stations whose concurrent CO and NO_x measurements were considered in this study are shown on the map.

None of the inventories is able to reproduce the observed CO/NO_x molar ratio for Santiago. If, according to inverse modeling exercises (e.g., Saide et al., 2011; Jorquera and Castro, 2010), CO emissions are globally overestimated by only 8–24%, then the NO_x emissions from mobile sources for 2000 (CENMA, 2000) and 2005 (DICTUC, 2007) should be overestimated by a factor of about 3 and 2 respectively. An overestimate of NO_x emissions is indirectly supported by current photochemical modeling applications over Santiago for which NO_x emissions must be reduced by a factor of up to 2 to avoid the complete titration of ozone (e.g., Schmitz et al., 2008).

The corresponding molar ratio of the disaggregated emissions for year 2000 is shown in Fig. 2 (lower panel). Highest (~20) values are generally located in the northeastern part of the city that corresponds to the wealthiest area, with largest motorization rates (~1000 vehicles/1000 inhabitants). Lowest (~6) are found among the lower income areas to the west of the basin reflecting the predominance of buses as the major mean of transportation. The corresponding ratios derived from the observations show changes of roughly only 10–20% among these different areas. These discrepancies between molar ratios based on observations and based on the inventories might be greater given that the CO inventory is considered to be overestimated downtown and underestimated towards the east of Santiago (e.g., Schmitz, 2005; Jorquera and Castro, 2010; Saide et al., 2011).

4.4. São Paulo

Ambient CO/NO_x ratios in São Paulo present substantial variation between 2000 and 2010 (See Fig. 3) with an exponential decrease in the ratio of about 7%. The ratio calculated from the emission estimates does not vary significantly between 2000 and 2009. From 2005 the ambient and emission CO/NO_x curves became closer, especially for Congonhas station. This behavior can be explained by the improvement of the data regarding the number of vehicles (from 2005 on there was a correction in the registration of the fleet). Congonhas station is close to an avenue that connects the city with an important highway and the presence of trucks is a significant fraction of the light-duty fleet (approximately 15%). This proportion is better captured at this site than that used in the emission ratio calculation. Ibirapuera and São Caetano do Sul presented a higher ratio when comparing emission and ambient data. At these stations, emissions are related to the light vehicle fleet emission. According to the ambient data there was a decrease in the emission of CO because the emission of NO_x has not varied substantially as the heavy duty fleet has not changed. CO mixing ratios have in fact decreased over the decade at all stations in São Paulo, whereas NO_x observations show no significant trend. This suggests that the change in CO/NO_x ratios is due a decrease in CO emissions from mobile sources, the same behavior found at Santiago.

4.5. Intercomparison of emission estimates

We compare different emission estimates of CO and NO_x, and the corresponding molar ratios for different cities when observations are available. Previous modeling studies have shown consistent CO total emissions as estimated using static inventories at Buenos Aires (e.g., Torres et al., 2010), Santiago (e.g., Saide et al., 2011; Jorquera and Castro, 2010) and São Paulo (e.g., Vivanco and

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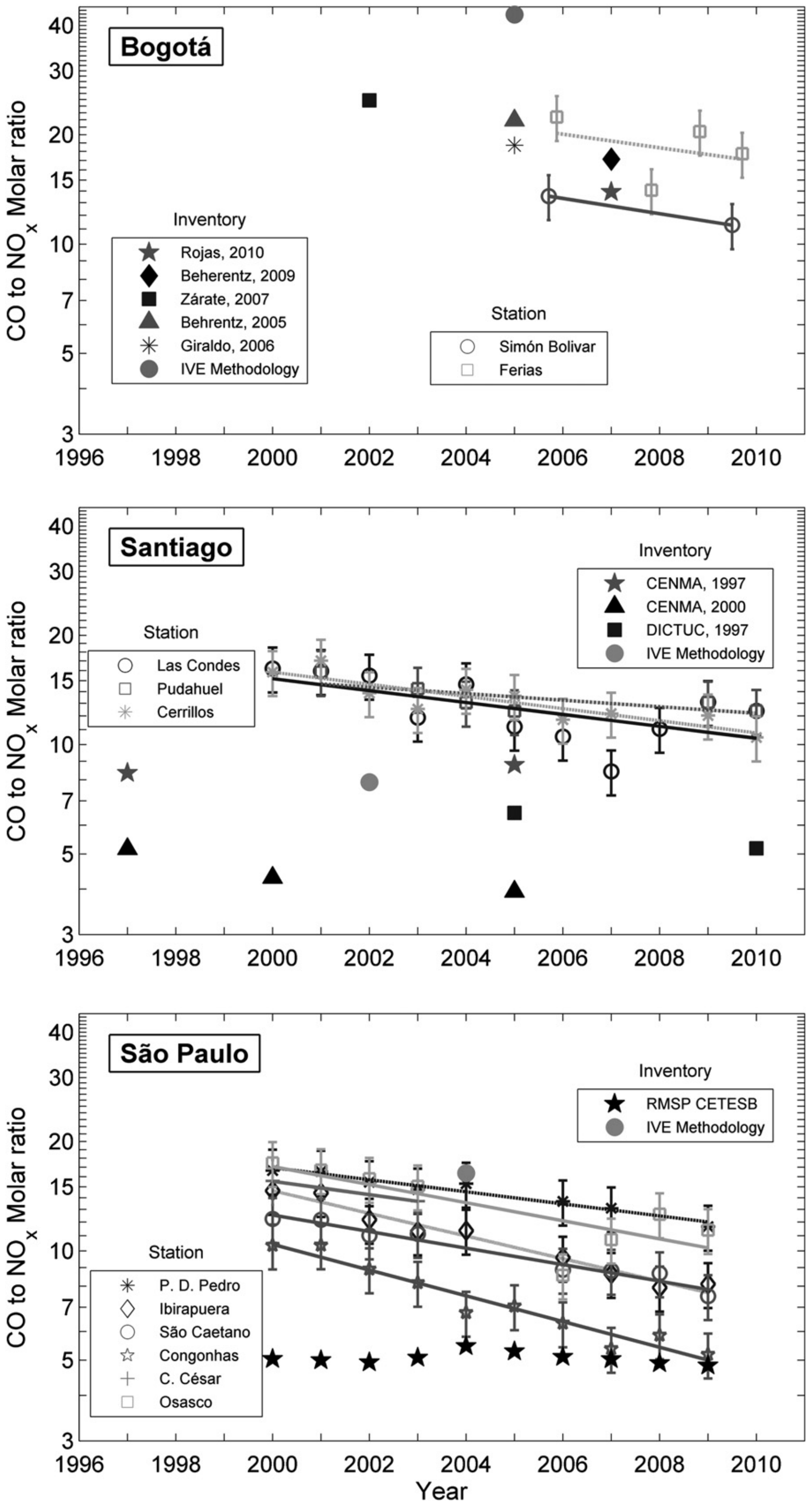

Fig. 3. CO to NO$_x$ emission ratios on a logarithmic scale from observations and emission estimates for Bogotá (Colombia) in the upper panel, Santiago (Chile) in the middle panel and São Paulo (Brazil) in the lower panel.

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Andrade, 2006; Martins et al., 2006). Using these results it may be established that Santiago and São Paulo show a drastic overestimate of NO_x by a factor 2 to 3 and by a factor 2, respectively, while Buenos Aires shows a 20% overestimate of NO_x.

Current emission estimates for Bogotá (Behrentz et al., 2009; Rojas et al., 2010) have not been independently evaluated for CO, which precludes inferring whether NO_x is under or overestimated. Nevertheless, we suspect that CO emissions might be overestimated because the values are substantially higher than those of Buenos Aires, which is a larger city with twice the fleet of Bogotá (1.2 million units). Also, Zárate et al. (2007) tested their inventory by means of dispersion modeling finding consistent CO emissions at a much lower rate, and five years seem not be enough to explain the discrepancy by changes in technology or fleet composition. Differences in air-fuel ratios due to the effect of altitude may explain part of the relative increase in CO emissions, but the magnitude of such effect is still uncertain and has not been well documented in Bogotá. Neither can this difference be explained by the fraction of gasoline driven vehicles, which is larger in Bogotá (88%) than in Buenos Aires (65%).

The IVE methodology seems to greatly overestimate CO emissions at all cities. Since CO emissions are mainly attributed to one category of vehicles (gasoline), and activity data are well described by the IVE approach, the reason for the overestimate appears to be related to emission factors used for CO. NO_x emissions estimated with IVE at Buenos Aires and São Paulo show a better correspondence with the values derived from observations. Santiago's results show a stronger overestimate than that of the official inventory. It is well known that estimating emissions of NO_x is more difficult than for CO. This is due to large uncertainties regarding activity data of light and heavy duty vehicles, in addition to uncertainties in emission factors, particularly in the case of static inventories that usually assume a simple mean velocity dependence.

Parrish et al. (2009) compare CO to NO_x molar ratios measured in megacities in the United States (6.7), Beijing (41), Ciudad de México (11) and Tokyo (8.5). Current Bogotá, Santiago and São Paulo show ratios of ca. 12, 10 and 11 respectively, i.e., molar ratios similar to those of Ciudad de México. Buenos Aires shows a molar ratio of 6.9 comparable to that of the cities in the United States. In all cities, the rate of change over the last 10–15 years resembles that of cities in the United States, suggesting a strong reduction in CO emissions. For Santiago and São Paulo the decrease in CO is confirmed by observed trends in CO levels and by independent dispersion modeling exercises.

5. Summary and conclusions

We have applied a methodology based on concurrent observations of CO and NO_x mixing ratios during the morning rush hour to evaluate emission estimates of these species related to traffic sources for Bogotá (Colombia), Buenos Aires (Argentina), Santiago (Chile), and São Paulo (Brazil). In all cities, the morning rush hour CO to NO_x molar ratios show substantial decreases over the last 10–15 years. In Santiago and São Paulo, the decline in the CO to NO_x molar ratio is related to a lowering of CO emissions, which in turn is reflected in declining CO ambient concentrations. The lack of accessible long-term CO and NO_x observations for Buenos Aires precludes a definite statement in this respect. However, it appears plausible that the decline is due to technological changes resulting in lower CO emissions. In Bogotá, part of the observed trend may be explained by fuel shifting in stationary sources, and part by changes in fleet composition.

It is worth noticing that the decline in CO emissions that follow from improved technologies may be counteracted in the future by growing motorization, including heavily polluting two-wheelers. Inspection and maintenance is central to ensure and speed up the integration of cleaner vehicle technologies, and the success of environmental policies. Although new cars in Bogotá, Santiago and São Paulo are obliged to comply with more stringent emissions standards, the fleet renewal is slower than the pace at which new cars are introduced, while motorization rates keep growing.

The observed CO to NO_x molar ratios are not captured by available inventories in the cities considered in this study. Comparison among inventories suggests that major uncertainties are linked to inadequate emission factors for CO, and inadequate activity data for light and heavy duty vehicles for NO_x. Since independent modeling studies have assessed CO emissions at Buenos Aires, Santiago and São Paulo, the present analysis allows inferring that current NO_x emissions are overestimated by a factor of up to 3 in Santiago and São Paulo, while Buenos Aires shows a relatively slight overestimate by 20%. In the case of Bogotá, we suspect that the current CO emission inventory is also overestimated. These results show the need of improving and systematically reviewing emission estimates, particularly those related to the growing mobile sources in our cities.

The use of ethanol-gasoline blends in São Paulo and Bogotá and of CNG in Buenos Aires and Bogotá appears to significantly decrease CO emissions. However, the reconversion of gasoline cars to be able to use CNG result in increased NO_x emissions.

Current air quality networks in Bogotá, Santiago, and São Paulo provide valuable information. However, more careful attention must be paid to calibration and continuity of the stations. Measurements of VOCs are not speciated, greatly limiting its usefulness to address mobile emissions, alternative fuel usage, photochemistry, etc. It is important to stress that quality control, calibration procedures, and concurrent meteorological data are indeed needed to make full use of these expensive networks. Also, accessibility to observations and emission data is crucial and it makes it easier to improve those databases.

Regarding the complex building of emission inventories, particularly for the key transportation sector, it is useful to carry out the type of exercise shown in this work, and to intercompare different approaches. The improvement of locally representative emission factors and activity data are pivotal to count on representative and reliable emission estimates. Shifting from the traditional average speed approach for estimating vehicle emissions to a vehicle power approach might help improving current estimates. Also, a better characterization of traffic conditions, and not only those of peak hours may help to better estimate mobile emissions in general. Improving mobile emission estimates is a crucial step to address air quality problems in South America and elsewhere.

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