

1 **EVALUATION OF VEHICLE EMISSION INVENTORIES FOR CARBON MONOXIDE AND**
2 **NITROGEN OXIDES FOR BOGOTÁ, BUENOS AIRES, SANTIAGO, AND SÃO PAULO**

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18 **Abstract**

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

31 **Key words:** Urban mobile emissions, CO, NO_x, South America

32 **1) Introduction**

33 In South American megacities, relatively inaccurate emission inventories and simple
34 emission-receptor models have been used to define curbing measures, mostly dealing

1 with industrial sources, and focusing on acute health impacts. As environmental
2 objectives become more ambitious, considering for instance chronic health effects,
3 addressing secondary particles or considering climatic impacts, the need for cost-
4 effective measures requires of more reliable and locally representative emission
5 inventories. According to current inventories, traffic emissions are responsible for 1/3 to
6 2/3 of the direct emissions of inhalable particles, and for the vast majority of ozone
7 precursors (See references in Section 2). Emission estimates are generally very difficult
8 to make, and this is particularly cumbersome in the case of mobile emissions for which
9 one must consider fuel type and consumption, vehicle technology and the conditions of
10 use for very heterogeneous fleets (e.g., Smit et al, 2010).

11 In this work, we evaluate emission estimates for mobile emissions of carbon
12 monoxide (CO) and nitrogen oxides (NO_x), including nitric oxide (NO) and nitrogen
13 dioxide (NO₂), in terms of their consistency with observations. We follow the approach
14 by Parrish et al. (2002), i.e., we compare the morning peak concentration ratios of CO
15 and NO_x with the corresponding emission ratios for mobile sources. In this approach it
16 is assumed that morning peak concentrations respond mostly to local emissions because
17 atmospheric mixing is relatively unimportant at these hours. Then, for stations where
18 mobile sources dominate, concentrations should reflect fresh mobile emissions, in
19 particular those of CO and NO_x. A similar approach was previously used by Vivanco
20 and Andrade (2006) to analyze emission estimates for São Paulo. Bogo et al (2001) and
21 Reich et al (2006) did analyze CO to NO_x ratios in Buenos Aires but considering all
22 data, not just the morning rush hour.

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

29 **2) Mobile emission estimates for selected South American cities**

30 CO emissions originate from incomplete combustion of fuel, and they are higher for
31 gasoline vehicles than for diesel vehicles (e.g., Heywood, 1988). NO_x emissions are
32 associated to high-temperature and high-oxygen processes, and they occur mainly in the

1 form of NO but in diesel vehicles NO₂ can constitute a significant fraction of NO_x
2 (~30%) (e.g., Heywood, 1988).

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

12 Compressed natural gas (CNG) is widely used as fuel for light-duty vehicles in
13 Argentina since the mid 90's, adding up to 14% of the fleet (D'Angiola et al, 2010). In
14 Bogotá, 7% of the fleet uses CNG. Santiago and São Paulo show a relatively negligible
15 number of CNG vehicles. Gasoline cars have been converted to use gasoline and CNG,
16 which is not optimal in terms of engine functioning and emissions. D'Angiola et al
17 (2010) analyzed the impact of the introduction of CNG in Buenos Aires finding, among
18 other things, that it has reduced the emission levels of CO and increased NO_x emissions.

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

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

28 a) Bogotá

29 Zárate et al (2007) estimated emissions for base year 2002 for particulate matter
30 (PM), CO, NO_x, volatile organic compounds (VOCs), sulfur dioxide (SO₂), methane
31 and carbon dioxide. Giraldo et al (2006) estimated mobile emissions using the IVE
32 model, including motorcycles. The most recent version of the emission inventory for
33 Bogotá is for base year 2007 (Behrentz et al, 2009). These authors used on-board

1 measurements to infer emission factors for PM, CO, NO_x and VOCs from mobile
2 sources. Rojas et al. (2010) completed this inventory adding diesel vehicles, and
3 disaggregated them in a spatial grid of 1x1 km².

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

7 b) Buenos Aires

8 A first inventory for Buenos Aires estimated CO, NO_x, VOCs, PM and SO₂
9 emissions for 1996 (Weaver and Balam, 1999). Mazzeo and Venegas (2003) reported
10 CO and NO_x without specifying the year of the inventory. The most recent and
11 complete emission estimate for mobile sources is the one by D'Angiola et al. (2010).
12 CO emissions are dominated by PCs older than 6 years old without catalytic converters
13 or with systems out of maintenance. NO_x emissions are dominated by the heavy-duty
14 vehicles (HDVs) that account with 34% of the emissions, followed by PCs, suburban
15 vehicles and taxis using CNG with 20%, and by gasoline PCs emitting the 13%.

16 c) Santiago

17 Environmental authorities have supported the formulation of emission inventories for
18 base years 1997, 2000, and 2005, and a projection for 2010 (CENMA, 1997; CENMA,
19 2000; DICTUC, 2007). Mobile emissions were estimated according to a bottom-up
20 methodology (Corvalán et al, 2002). In general, on-road mobile emissions of CO are
21 dominated by gasoline vehicles (>90%), mainly PCs. NO_x emissions are mainly
22 attributed to gasoline and diesel being the fraction attributed to diesel 53% in the 2010
23 inventory and 66% in the 2000 inventory for NO_x

24 In this study, we use the spatially disaggregated inventory described in Saide et al
25 (2011). It must be pointed out that even though total emissions are readily available
26 over the Internet, the disaggregated emission inventory is not.

27 d) São Paulo

28 According to the emission estimates provided by Environmental Agency of the State
29 of São Paulo (CETESB, 2010), between 2001 and 2009, CO emissions have declined by
30 7%, with the largest reduction occurring in 2005 when there was a correction in the
31 methodology for obtaining the total number of vehicles. The official inventory for the

1 light fleet is calculated based on the measurements of emissions factors in a
2 dynamometer for new vehicles and then multiplied by an aging factor according to the
3 age of the fleet. How many kilometers the light and duty fleets run each day on average
4 is also considered. This inventory is not spatially disaggregated. NO_x emissions also
5 diminished between 2001 and 2009 but only by 3%. The evaluation of the emission
6 inventory for diesel trucks and buses is performed based on data from type of motor, in
7 g/kWh.

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

19 **3) CO and NO_x observations**

20 We have used hourly averaged data compiled by the official monitoring networks in
21 Bogotá, Santiago and São Paulo. In the case of Buenos Aires, due to a lack of access to
22 historical data, we complemented one year of official data with data collected at one
23 monitoring site located in front of a high-way. These data were subject to various
24 quality control checks. After a careful visual observation of the data series, extreme
25 values were suppressed from the database by excluding the 2 percentile upper and lower
26 tails of the distribution of the logarithm of the values. The time series were also checked
27 with respect to the detection limit of the instruments, which is nevertheless usually
28 below the lower 2-percentile cut. To ensure capturing the seasonal and diurnal cycles,
29 we only kept years and stations for which we had 75% of completeness every eight
30 hours for each day and 75% of the data for each season of the year. Diurnal cycles of
31 CO and NO_x mixing ratios were compared to diurnal traffic activity data to identify the
32 morning peak in CO and NO_x that could be attributed to mobile sources. The
33 application of these filtering criteria precluded the use of Bogotá data for a multi-year

1 analysis due to the discontinuity of the data and calibration problems. Similar problems
2 but to a lesser extent were found at all cities. This highlights the need for improvement
3 and more careful quality control in present monitoring networks. A summary of the
4 characteristics of the stations considered in this study is shown in Table 1.

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

12 During the last twenty years, institutions have performed air quality measurements in
13 the Buenos Aires region in an uncoordinated manner, resulting in fragmented and scarce
14 information. For this work, we obtained from city officials one year of CO and NO_x
15 hourly data, for 2009. The corresponding monitoring site, named Centenario and located
16 at the center of the city, is characterized for a dense vehicular traffic. We complemented
17 the official data set with a two month monitoring campaign at a site (CNEA) located in
18 front of a highway located in the border between the city itself and the neighboring
19 districts. The CNEA monitoring site was located at a height of 8 meters above the
20 ground. Non-dispersive infrared absorption was used to continuously measure CO with
21 a HORIBA monitor, model APMA-360 using a gas standard of 12.5 ppm to fix the span
22 scale calibration. Chemiluminescence was used to measure NO_x also in continuous
23 manner, with a HORIBA monitor APNA-360 calibrated with a gas standard of NO of
24 5.06 and 99.7 ppm diluted with a 1:10000 ratio by means of a SGGU-514 dilutor
25 device. A marked diurnal cycle is apparent from the observations available at Buenos
26 Aires following vehicle activity (See Figure 1). While these data do not show a marked
27 seasonal pattern, historical data show higher concentrations from May to October than
28 in the hot summer months.

1 CO and NO_x have been concurrently measured at three stations in Santiago since
2 2000 by the regional office of the Ministry of Health. All stations show a marked
3 seasonal cycle with highest concentrations of CO and NO_x in winter. A strong diurnal
4 cycle is also apparent. Cerrillos and Pudahuel stations, located in low income industrial
5 and residential areas to the south-west and west of the basin, show two maxima. A sharp
6 morning maximum around 8 AM and a broad maximum in the late afternoon and
7 evening hours centered at 7 PM. Las Condes, a high-income area to the north-east of the
8 city, shows a primary morning maximum around 9 AM and a secondary maximum in
9 the mid-morning. The evening maximum is broader at Las Condes than in Cerrillos and
10 Pudahuel. These behaviors follow on the one hand, the diurnal cycle of emissions,
11 mainly mobile sources discussed earlier, and on the other hand, from the characteristic
12 radiatively driven air circulation of the Santiago basin, with very stable nights and
13 nearly calm conditions, and south-westerly light winds during the afternoon. The latter
14 partially explains the broader evening peak observed at Las Condes. The mixing
15 conditions result in a very depressed or collapsed boundary layer during nighttime,
16 particularly in winter and a convective layer in the afternoon hours, particularly in
17 summer.

18 In São Paulo air pollution monitoring started in late 1972 with 14 stations for
19 measurement of black smoke and SO₂ under the responsibility of CETESB. Nowadays
20 21 automatic stations are in operation in the Metropolitan Area of São Paulo, and 40
21 automatic and 47 manual in São Paulo state. The highest concentrations of CO and NO_x
22 occur during winter, which is characterized as a dry period, with clear skies, subsidence
23 and thermal inversions. There is also an increase in the concentrations during the night
24 due to increased atmospheric stability.

25 **4) Results**

26 a) Bogotá

27 Although the air quality monitoring network has been active for more than a decade,
28 only the period between 2005 and 2010 was considered to have the appropriate quality
29 to observe the trend in measured CO/NO_x ratio and compare it with that from emission
30 inventories. Ambient CO/NO_x ratio decreased in both Ferias and Simón Bolívar stations
31 at a similar rate, but its values were consistently and significantly higher in the Ferias
32 station.

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

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

19 b) Buenos Aires

20 Both CNEA and Centenario monitoring stations show similar ambient CO to NO_x
21 molar ratios, i.e., (6.9±1.0) and (6.2±0.9) respectively (See Figure 1). Bogo et al (2001)
22 and Reich et al (2006) obtained a ratio of roughly 14 using measurements from 1999
23 and 2001 respectively. Three reasons may explain this difference: (1) the increased use
24 of natural gas by the fleet of Buenos Aires, mainly in cars and light duty vehicles; (2)
25 the monitoring sites of previous studies were located near or in front of streets with a
26 low influence of heavy duty vehicles (trucks and coaches) that usually burn diesel oil
27 and represents the 40% of the total NO_x Buenos Aires Metropolitan Area emissions,
28 whereas the sites considered in this work are closer to the average circulating fleet; and
29 (3), in previous works, authors included all the hours of the day, while here we are
30 including only the morning peak concentration ratios. Measurements at CNEA in 2010

1 and at Centenario in 2009 are consistent with the inventory ratio for the year 2006, for
2 which a value of (6.6 ± 1.7) was obtained. In Figure 2 (middle panel) the CO/NO_x molar
3 ratio is presented spatially disaggregated showing a range from 1 to 12 where the lower
4 values correspond to highways with trucks and coaches burning diesel as the main
5 emitters, and higher values in areas where heavy diesel vehicles are absent in the
6 inventory. Obtaining a similar ratio at CNEA and Centenario is a somewhat surprising
7 since CNEA is located by a highway with a larger contribution of diesel vehicles than
8 that of Centenario. This suggests that the categorized activity data requires further
9 refinement.

10 c) Santiago

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

25 None of the inventories is able to reproduce the observed CO/NO_x molar ratio for
26 Santiago. If, according to inverse modeling exercises (e.g., Saide et al 2011; Jorquera
27 and Castro, 2010), CO emissions are globally overestimated by only 8 to 24%, then the
28 NO_x emissions from mobile sources for 2000 (CENMA, 2000) and 2005 (DICTUC,
29 2007) should be overestimated by a factor of about 3 and 2 respectively. An
30 overestimate of NO_x emissions is indirectly supported by current photochemical

1 modeling applications over Santiago for which NO_x emissions must be reduced by a
2 factor of up to 2 to avoid the complete titration of ozone (e.g., Schmitz et al, 2008).

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

14 d) São Paulo

15 Ambient CO/NO_x ratios in São Paulo present substantial variation between 2000 and
16 2010 (See Figure 3) with an exponential decrease in the ratio of about 7%. The ratio
17 calculated from the emission estimates does not vary significantly between 2000 and
18 2009. From 2005 the ambient and emission CO/NO_x curves became closer, especially
19 for Congonhas station. This behavior can be explained by the improvement of the data
20 regarding the number of vehicles (from 2005 on there was a correction in the
21 registration of the fleet). Congonhas station is close to an avenue that connects the city
22 with an important highway and the presence of trucks is a significant fraction of the
23 light duty fleet (approximately 15%). This proportion is better captured at this site than
24 that used in the emission ratio calculation. Ibirapuera and São Caetano do Sul presented
25 a higher ratio when comparing emission and ambient data. At these stations, emissions
26 are related to the light vehicle fleet emission. According to the ambient data there was a
27 decrease in the emission of CO because the emission of NO_x has not varied substantially
28 as the heavy duty fleet has not changed. CO mixing ratios have in fact decreased over
29 the decade at all stations in São Paulo, whereas NO_x observations show no significant
30 trend. This suggests that the change in CO/NO_x ratios is due a decrease in CO emissions
31 from mobile sources, the same behavior found at Santiago.

1 e) Intercomparison of emission estimates

2 We compare different emission estimates of CO and NO_x, and the corresponding
3 molar ratios for different cities when observations are available. Previous modeling
4 studies have shown consistent CO total emissions as estimated using static inventories
5 at Buenos Aires (e.g., Torres et al, 2010), Santiago (e.g., Saide et al, 2011 a Jorquera
6 and Castro, 2010) and São Paulo (e.g., Vivanco and Andrade, 2006; Martins et al,
7 2006). Using these results it may be established that Santiago and São Paulo show a
8 drastic overestimate of NO_x by a factor 2 to 3 and by a factor 2, respectively, while
9 Buenos Aires shows a 20% overestimate of NO_x.

10 Current emission estimates for Bogotá (Behrentz et al, 2009; Rojas et al, 2010) have
11 not been independently evaluated for CO, which precludes inferring whether NO_x is
12 under or overestimated. Nevertheless, we suspect that CO emissions might be
13 overestimated because the values are substantially higher than those of Buenos Aires,
14 which is a larger city with twice the fleet of Bogotá (1.2 million units). Also, Zárata et al
15 (2007) tested their inventory by means of dispersion modeling finding consistent CO
16 emissions at a much lower rate, and five years seem not be enough to explain the
17 discrepancy by changes in technology or fleet composition. Differences in air-fuel ratios
18 due to the effect of altitude may explain part of the relative increase in CO emissions,
19 but the magnitude of such effect is still uncertain and has not been well documented in
20 Bogotá. Neither can this difference be explained by the fraction of gasoline driven
21 vehicles, which is larger in Bogotá (88%) than in Buenos Aires (65%).

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

32 Parrish et al (2009) compare CO to NO_x molar ratios measured in megacities in the
33 United States (6.7), Beijing (41), Ciudad de México (11) and Tokyo (8.5). Current
34 Bogotá, Santiago and São Paulo show ratios of ca. 12, 10 and 11 respectively, i.e.,

1 molar ratios similar to those of Ciudad de México. Buenos Aires shows a molar ratio of
2 6.9 comparable to that of the cities in the United States. In all cities, the rate of change
3 over the last 10 to 15 years resembles that of cities in the United States, suggesting a
4 strong reduction in CO emissions. For Santiago and São Paulo the decrease in CO is
5 confirmed by observed trends in CO levels and by independent dispersion modeling
6 exercises.

7 **5) Summary and conclusions**

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

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

27 The observed CO to NO_x molar ratios are not captured by available inventories in the
28 cities considered in this study. Comparison among inventories suggests that major
29 uncertainties are linked to inadequate emission factors for CO, and inadequate activity
30 data for light and heavy duty vehicles for NO_x. Since independent modeling studies
31 have assessed CO emissions at Buenos Aires, Santiago and São Paulo, the present
32 analysis allows inferring that current NO_x emissions are overestimated by a factor of up
33 to 3 in Santiago and São Paulo, while Buenos Aires shows a relatively slight

1 overestimate by 20%. In the case of Bogotá, we suspect that the current CO emission
2 inventory is also overestimated. These results show the need of improving and
3 systematically reviewing emission estimates, particularly those related to the growing
4 mobile sources in our cities.

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

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

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

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47 evaluate emission inventories. *Atmospheric Environment*, 41, 29, 6302-6318.

1 **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	Ferías	-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 high-way
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

2

1 **Figure Captions**

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

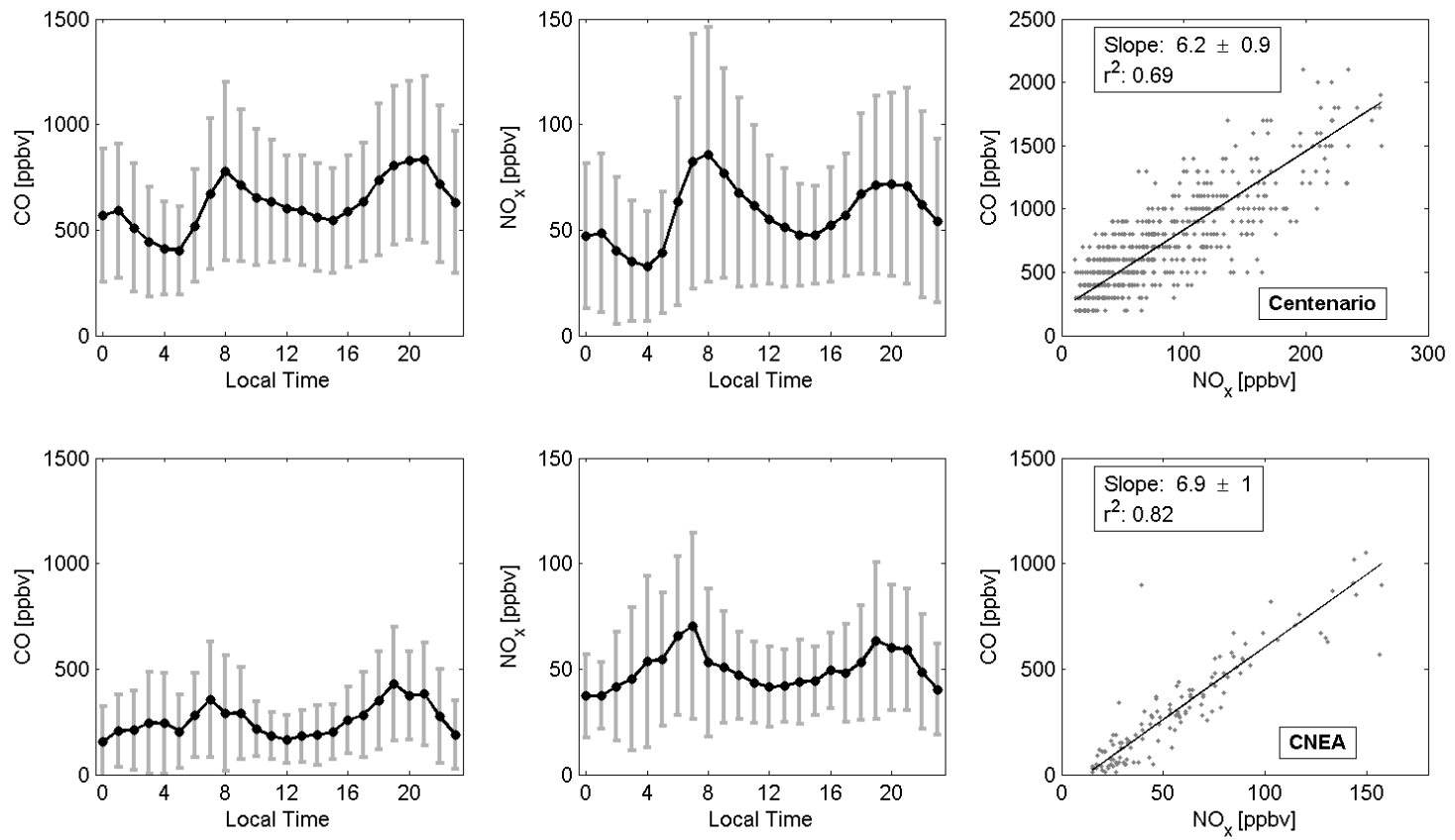
8
9 **Figure 2.** Disaggregated emissions of CO (in g CO/km² s, left panels) and NO_x (in
10 gNO_x/km² s, assuming 90% NO and 10% NO₂) middle panels, and the corresponding CO
11 to NO_x molar ratio (right panels), for Bogotá (upper panel), Buenos Aires (middle panel),
12 and Santiago (lower panel). The location of the monitoring stations whose concurrent CO
13 and NO_x measurements were considered in this study are shown on the map.

14
15 **Figure 3.** CO to NO_x emission ratios on a logarithmic scale from observations and
16 emission estimates for Bogotá (Colombia) in the upper panel, Santiago (Chile) in the
17 middle panel and São Paulo (Brazil) in the lower panel.

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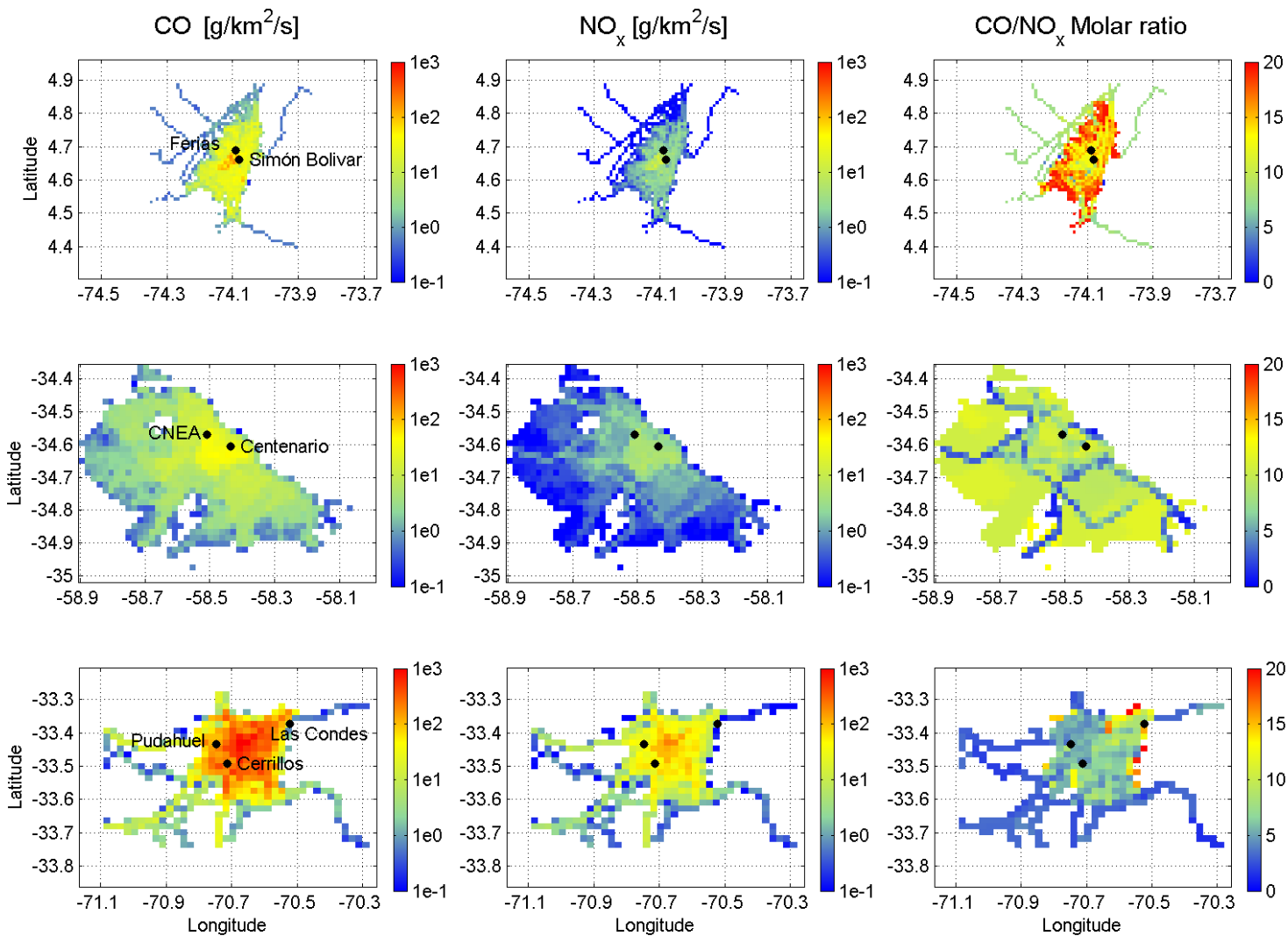
1 **Figure 1.**



2

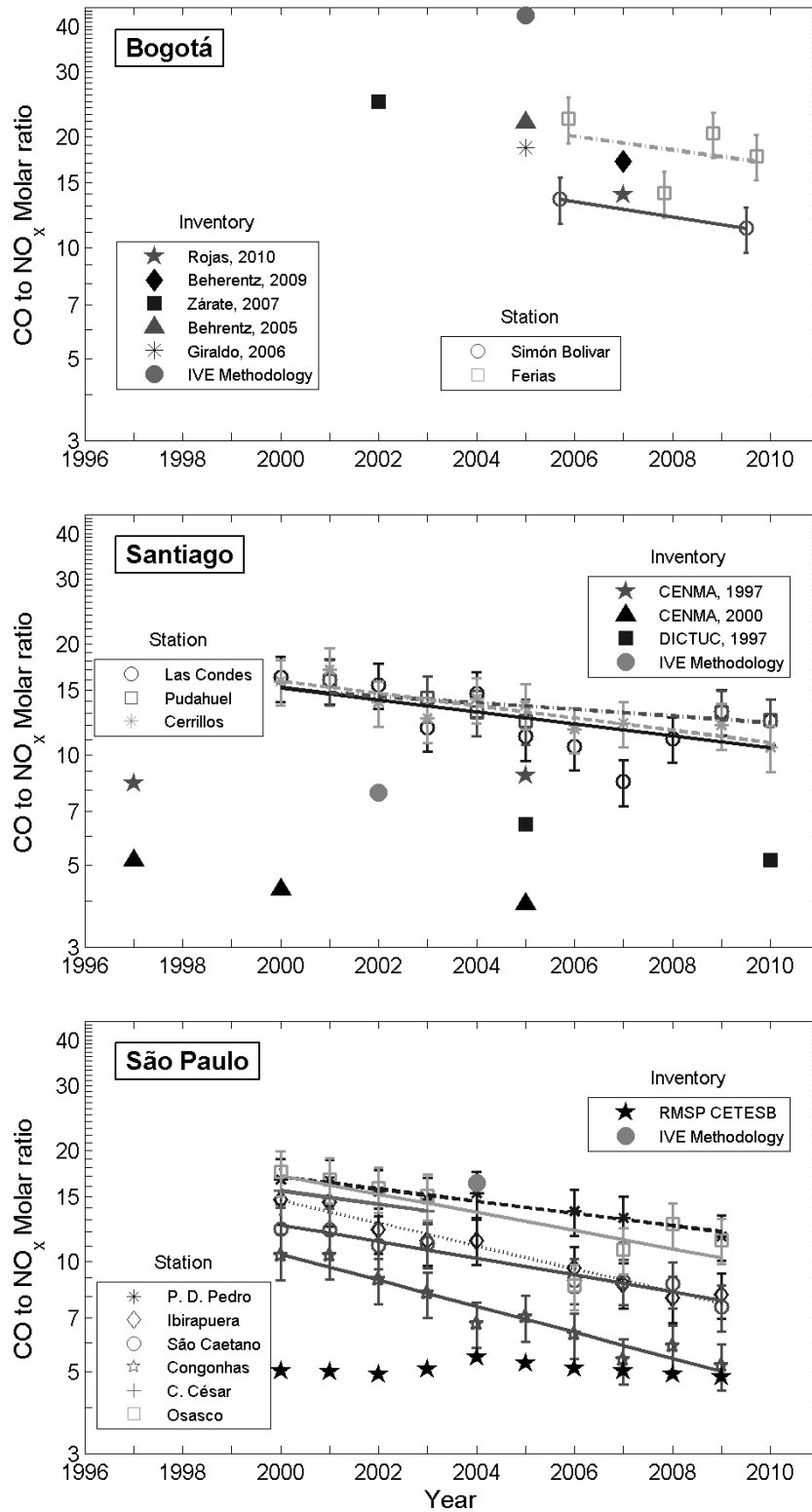
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1 **Figure 2.**



2

1 **Figure 3.**



2