Chapter 18

Bioethanol and Biodiesel as Vehicular Fuels in Brazil — Assessment of Atmospheric Impacts from the Long Period of Biofuels Use

Thiago Nogueira, Denise de Sales Cordeiro,
Rodrigo Alejandro Abarza Muñoz,
Adalgiza Fornaro, Antonio H. Miguel and
Maria de Fatima Andrade

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1. Introduction

The research field on alternative fuels has been developed in order to reduce the current dependence on petroleum derivatives and to improve air quality. Since the transportation sector represents one of the largest contributions to greenhouse gas (GHG) and other gas pollutants inventories, increasing the use of renewable fuel potentially reduces GHG emissions, such as carbon dioxide (CO_2), which contribute to global warming and climate change [1, 2]. Brazil is an important scenario for the study of environmental impact from the large-scale use of biofuels because a significant fraction of the vehicular fuels is derived from biomass (ethanol and biodiesel). In Brazil, anhydrous ethanol (maximum water mass content 0.7%) is added as an anti-knock additive to regular gasoline at a concentration ranging from 20% to 25% (known as gasohol or Gasoline C, E20, or E25 in Europe). Hydrous ethanol (maximum water concentration of 7.4%) is also used as a fuel in light-duty vehicles (LDV). Additionally, Brazil has experienced the use of biodiesel as additive to regular diesel since 2008. The minimum biodiesel content was set to 2% in 2008 and this content has been increasing, reaching 10% in 2015.

1.1. Bioethanol and biodiesel: The main biofuels in Brazil

Ethanol biofuel has characteristics that favor cleaner combustion, therefore reducing the emission of air pollutants. Ethanol is produced from the fermentation of agricultural products

such as sugar cane, corn, wheat, beet, and cassava. The vast majority of ethanol produced worldwide is from sugar cane, mainly in Brazil [3]. Biodiesel consists of long-chain fatty acids esters mixture, which is produced by transesterification reaction of triglycerides present in vegetable oils or animal fats with short-chain alcohols in the presence of a catalyst (normally a base such as sodium (NaOH) or potassium (KOH) hydroxide) [4]. Figure 1 shows transesterification reactions of triglycerides for biodiesel production.

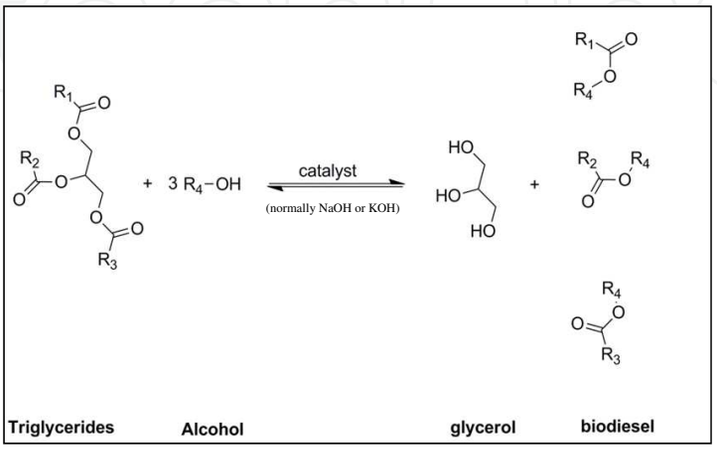

Figure 1. Transesterification reaction of triglycerides for biodiesel production.

Biodiesel use has been stimulated as an environmentally favorable alternative, since many studies have shown that biodiesel blends reduce particulate matter (PM), carbon monoxide (CO), and total unburned hydrocarbon (THC) emissions compared to diesel fuel [1, 5-8]. Biodiesel blends have been shown to reduce the overall life cycle emissions of CO_2, when evaluated using a total carbon life cycle analysis [1, 9], although this can depend on a variety of factors, such as land use change and transportation [10, 11]. A drawback in using biodiesel blends, however, is the potential to increase nitrogen oxide (NOx) emissions compared to ultra-low sulfur diesel fuel [5-7, 9, 12].

The Brazilian specification for biofuel is similar to the European and American, with some flexibility to meet the characteristics of domestic raw materials. The Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP) is the governmental agency that regulates fuels sold in Brazil through resolutions and technical specifications. The ANP resolution Nº 42 [13] provides a biodiesel specification (B100) according to the provisions contained in the Technical Regulation No. 4/2004. ANP Resolution Nº7 provides a specification for bioethanol (anhydrous and hydrous ethanol) according to the provisions contained in the Technical Regulation Nº 3/2011. Acceptable values or ranges for physical and chemical properties of both Brazilian biofuels, the respective analytical methods, and the importance of each analysis can be found on specialized literature [4, 14-16].

Biofuel analysis should be performed on a representative sample obtained according to the same methods described on ABNT NBR 14883 - Petroleum and petroleum products - Manual sampling or ASTM D 4057 - Practice for Sampling Petroleum and Liquid Petroleum Products

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(Practice for Manual Sampling of Petroleum and Petroleum Products) or ISO 5555 (Animal and vegetable fats and oils - Sampling). The monitoring of metals in bioethanol, such as iron and copper, is recommended by ANP as well as European and American norms, but not in biodiesel. Trace metals in biodiesel can catalyze oxidation processes which lead to the degradation of biodiesel and therefore this should be a parameter included in controlling parameters [15]. Inorganic anions such as chloride and sulfate in bioethanol can induce corrosion inside engine and storage tanks. Additionally, the monitoring of residual glycerol in biodiesel is related to the possible formation of acrolein, a pollutant known to cause severe adverse human health effects, from the burning of biodiesel containing glycerol. Glycerol is the main co-product formed during the production of biodiesel (Figure 1). Other impurities can be found in biodiesel such as residual alcohol, catalysts, and free fatty acids [17, 18].

Fuel quality, improvements in the technology applied to the engine, and the maintenance conditions are the main factors that influence the issuance of vehicle pollutants. To reduce emissions considerably, it is necessary to develop advanced combustion technologies and control devices, as well as environmentally clean fuels (with low pollution potential). Although many efforts have been done to develop environmentally friendly technologies and "clean fuels" to reduce environment pollution, vehicular emissions are still the main pollution source in many countries due to the increase in the urbanization and in the necessity of daily increase of displacements. Therefore, the development of public policies to reduce the contribution from this sector to air pollution becomes the priority for several urban areas. In the following, the historic overview of Brazilian biofuel uses and public programs of vehicular emissions control are addressed.

2. A historic overview of biofuels use in Brazil

In 1975, the Brazilian National Alcohol Program (Programa Nacional do Álcool - PROALCOOL) was created in Brazil to stimulate the use of domestic sources as a substitute for imported petroleum, and since then important changes occurred in the fuel composition used by motor vehicles in the country [19]. In 1979, 15% (v/v) of anhydrous ethanol started to be added to gasoline, reaching up to 22% (v/v) in the following years. The addition of 22% ethanol in gasoline was adopted by the Brazilian National Environment Council (CONAMA) [20] in 1990, on the recommendation of the energy sector. Production of ethanol-powered vehicles started in 1980.

The availability in the domestic market of hydrous ethanol and gasohol has brought benefits to the environment and to public health, highlighting the drastic reduction of toxic lead concentrations in the atmosphere. Ethanol acts as an anti-knock agent, replacing the lead-based additives, which have been completely removed from the national gasoline since 1991. In 1998, the Federal Government increased the content of anhydrous ethanol in gasoline to 24% through the Provisional Federal Law No. 1662-3 [21]. This increase did not result in significant changes in the vehicular emissions profile, since the vehicles manufactured in the country with more advanced technology, such as electronic fuel injection and oxygen sensors, were endowed with autocompensation system of the air/fuel ratio for variations of the ethanol

content of that order. In 2006, the country's fuel blenders had to reduce ethanol content to 20% of its blended fuel because of ethanol shortages and returning to 25% soon after. In Brazil, gasoline volume sold was constant at around 2 × 10^7 m^3 between 1996 and 2009 and then increased to 4 × 10^7 m^3 in 2013 (Figure 2). During that same period, ethanol sold decreased from 1996 to 2003, restarted to increase, which peaked in 2009 (at 1.6 × 10^7 m^3) and decreased to 1.2 × 10^6 m^3 in 2013 [22].

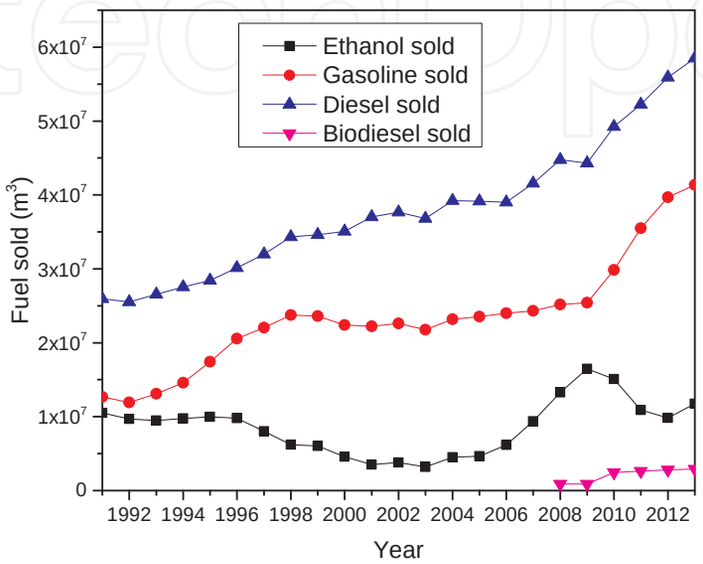

Figure 2. Fuel consumption in Brazil. Data from the Brazilian National Agency of Petroleum, Natural Gas and Biofuels [22]. The biodiesel consumption was calculated considering its minimum content in diesel: 2% in 2008-2009 and 5% 2010-2013.

During all periods shown in Figure 2, diesel sales increased 2.2 times, from 2.6 × 10^7 m^3 in 1991 to 5.8 × 10^7 m^3 in 2013. Biodiesel started to be sold in 2008, and since then sales increased from 0.9 × 10^6 m^3 to 2.9 × 10^6 m^3. In Brazil, the diesel composition has considerably changed in the last years. Diesel sold in Brazil, known as type B (containing biodiesel), the minimum biodiesel content was set to be 2% (v/v, B2) in 2008, 5% (v/v, B5) in 2010, 7% (v/v, B7) in 2014, and 10% (v/v, B10) after January, 2015. Details of the new regulations and for non-road applications are available at the ANP website [23].

The growth in the production of hydrous ethanol-fueled vehicles during the 1980s was very high due to the creation of the Brazilian National Alcohol Program, when about 94% of the new passenger vehicles were fueled by this biofuel, as can be seen in Figure 3. On the other hand, between the years 1989 and 1990, the surplus of gasoline associated with other factors resulted in a change from national alcohol overproduction to a deficit production situation [24]. In 1990, a combination of bad climatic conditions together with a rise in the international price of sugar forced the Brazilian Government to import alcohol (including methanol) for the first time to meet the national demand. Consumers had serious difficulties in getting alcohol to fill the tanks of their cars. In that year the production of ethanol-powered vehicles dropped from about 47% to about 11% of new vehicles produced. Due to shortage of anhydrous ethanol in Brazil, it was introduced, on an emergency basis, the mixture ethanol-gasoline-methanol

(7%-60%-33% by volume, respectively), for use in ethanol-powered vehicles. After 2003, flex fuel vehicles were introduced into the Brazilian market. These vehicles are designed to be fueled with gasohol, ethanol, or any blend of both. These vehicles had become attractive because their owners no longer had to be concerned with the price and market availability of ethanol. Increases in the pump price of ethanol lead to large-scale consumption of gasohol, and then of ethanol when ethanol prices subsequently fell to a competitive level. These vehicles types use special electronic sensors and an on-board computer to recognize the fuel composition and properly adjust the engine combustion parameters, without any interference from the driver. As shown in Figure 3, sales of these vehicles increased quickly in the Brazilian market. The vehicular industry in Brazil plays an important role on the economy, and has received governmental incentives. Currently, the government's role in ethanol fuels is much less and much different than in earlier times, and problems with the competition between the food and fuels sectors for sugarcane remain common.

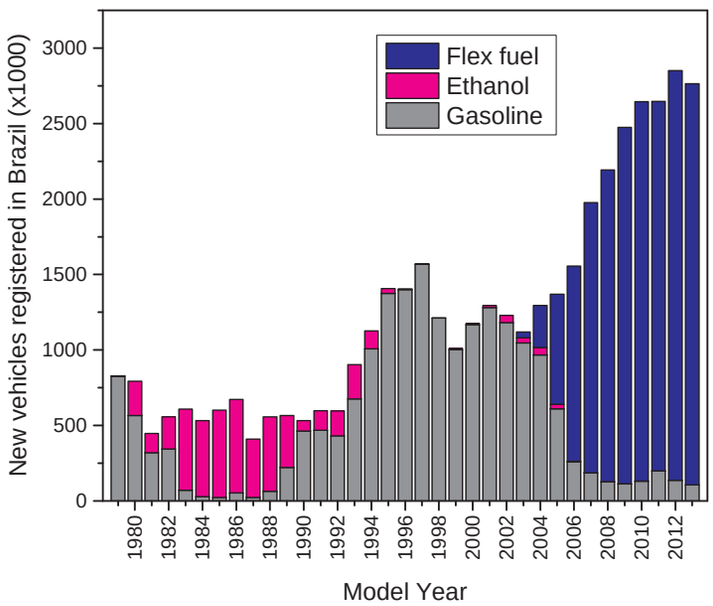

Figure 3. New light-duty vehicles registered in Brazil by fuel type. Data from the Associação Nacional dos Fabricantes de Veículos Automotores (ANFAVEA).

3. Brazilian vehicular emissions and control program of emissions

3.1. Light-duty vehicles emission controls

To control vehicular emissions, the Brazilian Government created in 1986 the Brazilian Motor Vehicle Air Pollution Control Program (PROCONVE) [20]. Its main goal was the reduction of atmospheric contamination by setting emission standards for vehicles, inducing technological improvements of manufacturing processes, enforcing those vehicles and engines to meet emission limits in standardized tests using a reference fuel. PROCONVE's target for control-

ling pollution from otto cycle LDV is based on the US Programs LEV (Low Emission Vehicle) and the California Air Resources Board (CARB) [25]. The compliance of requirements is assessed through protocols developed based on standardized dynamometer procedures and "reference fuels" trials. Furthermore, PROCONVE also imposes certification of prototypes and the statistical monitoring of vehicles in production (production trials). The PROCONVE program for LDV was performed at different phases that are described in Table 1.

Stage	Year of implementation	Description
Phase 1 (L-1)	1988-1991	Characterized by elimination of the most polluting vehicles and improvement of vehicles under production. The control of evaporative emissions also had begun at this stage. The main technological innovations that occurred in this phase were recycling of exhaust gases to control NOx emissions; secondary air injection in the exhaust manifold to control CO and HC; and optimization of the ignition stage.
Phase 2 (L-2)	1992-1996	Adaptation of catalysts and fuel injection systems for use with a mixture of ethanol was performed. The main innovations in vehicles were the electronic injection, electronically assisted carburetors, and catalytic converters. In 1994, the control of noise from vehicles started.
Phase 3 (L-3)	1997-2004	Given the requirement to meet the limits established from January 1, 1997 (CONAMA Resolution No. 15/1995), there were highly significant reductions compared to previous limits, and the manufacturer / importer employed the best available technology for the formation of mixing and electronic engine control, e.g., the oxygen sensor.
Phase 4 (L-4)	2005-2008	Referring to the CONAMA Resolution No. 315/2002, the priority at this phase that began in 2005 was the reduction of emissions of HCs and NOx (ozone precursor compounds). To attend this phase, engines with new technologies such as the optimized combustion chamber, increase in pressure of the injection pump, and the electronic fuel injection were developed.
Phase 5 (L-5)	2009-2013	The same emission limits of phase L-4 (CONAMA Resolution No. 315/2002) was applied at this phase. The priority in phase L-5 was to reduce emissions of HC and NOx. Analogous to the phase L-4, technological innovations were developed (optimization of combustion chamber, increase in pressure of the injection pump, and the improvement in the electronic fuel injection). At this phase there was a reduction of 31% in emissions of non-methane hydrocarbons (NMHC) for light vehicles. In addition, NOx emissions showed reduction of 48% and 42% for light vehicles and diesel-powered vehicles, respectively. Additionally, aldehyde emissions were reduced by approximately 67% for the light-duty vehicles.

Table 1. Phases during the implementation of Brazilian Motor Vehicle Air Pollution Control Program for light vehicles (PROCONVE-L) [20].

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Figure 4 shows the evolution of the vehicular emission limits of CO, HC, NOx, and total aldehydes (RCHO) for LDV (Phases PROCONVE -L). As noted, the phases become increasingly restrictive. For instance, in PROCONVE (L-1) new vehicles had to emit no more than 24 g of CO per kilometer traveled; this value decreased to 12 g/km in phase 2 (L-2) and remained at 2 g/km between phases 3 and 5, a reduction of approximately 92% in the emission of this pollutant. Nitrogen oxides had a gradual reduction during PROCONVE phases. In phase 1 (L-1), vehicles could emit a maximum of 2 g/km. This value was reduced to 1.4 g/km at L-2 (reduction of 30%). In subsequent phases, the reductions ranged between 52% and 58%. In phase 5, the maximum emission allowed for NOx from new vehicles was 0.12 g/km. Volatile organic compounds such as HC and RCHO also had a very significant reduction in emissions. In phase 1, the maximum emission of HC was 2.1 g/km, whereas in phase 5 this value was 0.05 g/km, a reduction of 98%. Limits were imposed to RCHO only in phase 2, when the maximum emission allowed for RCHO was 0.15 g/km in phase 2 and decreased to 0.02 g/km in phase 5, a reduction of 87%.

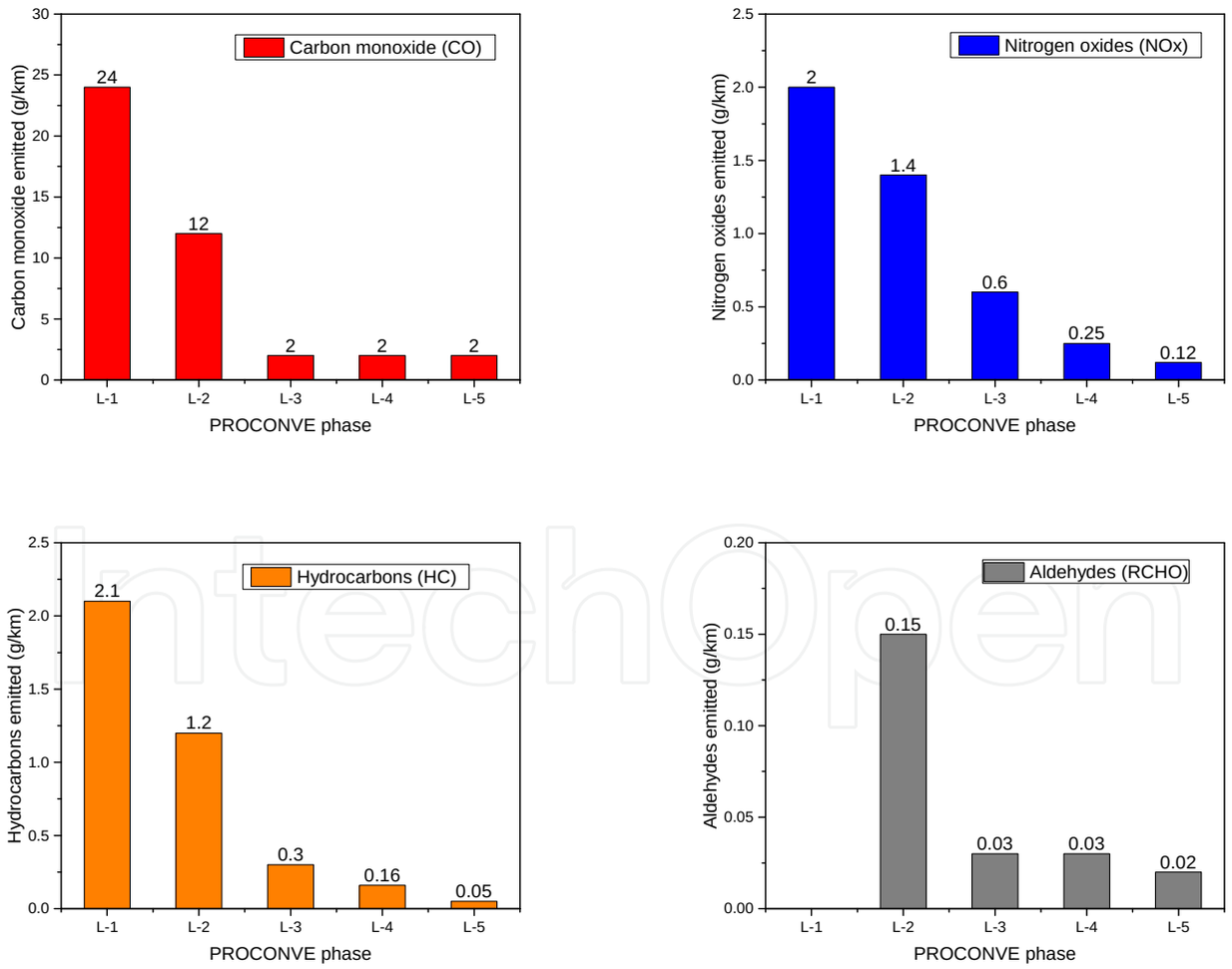

Figure 4. Evolution of the emission limits permit of CO, HC, NOx, and CHO for light vehicles during the phases of PROCONVE-L.

3.2. Heavy-duty vehicles emissions control

HDV have long been recognized as an important source of air pollution in urban areas [26, 27]. According to the São Paulo State Environmental Protection Agency [28], HDV are responsible for emitting into the atmosphere of Metropolitan Area of Sao Paulo 60.9% of all anthropogenic NOx, and 35.3% of all inhalable particulate matter (PM_{10}) during the 2012 year. HDV diesel-powered also contribute to emissions of fine particulate matter ($PM_{2.5}$), with black carbon (BC) as the main constituent. Emissions of CO and VOC, mainly aldehydes, also contribute to the air pollution from diesel exhaust [29, 30]. Efforts to reduce the emission of pollutants by HDV were delayed in Brazil. PROCONVE regulations for HDV began in 1990, but during phases 1 and 2 the limits for gaseous emission (P-1 phase) and PM (P-2 phase) were not legally required. The PROCONVE phases for controlling HDV emissions (Phases "P") are presented in Table 2 (CONAMA Resolution No. 18/86 [20]).

Stage	Year of implementation	Description
Phase P-1 and P-2	1990-1993	In 1990, engines with lower emission levels than that required in 1993 (the year that began the emission control for vehicles of this type with the introduction of phases P-1 and P-2) were produced. During this period, the limits for gaseous emission (P-1 phase) and particulate matter (P-2 phase) were not legally required.
Phase P-3	1994-1997	The development of new engine models aimed at the reduction of fuel consumption, to increase power and to reduce emissions of NOx by adopting the intercooler and turbo engines. This phase promoted a drastic reduction of CO (43%) and HC (50%).
Phase P-4	1998-2002	Emission limits have become even more restrictive than the P-3 phase.
Phase P-5	2003-2008	Aimed to reduce emissions of PM, NOx, and HC.
Phase P-6	2009-2011	In January 2009, the phase P-6 started, according to CONAMA Resolution No. 315/2002. The main objective of this phase, as well as the P-5 phase, was the reduction of emissions of particulate matter (PM), NOx, and HC.

Table 2. Phases for the implementation of Brazilian Motor Vehicle Air Pollution Control Program for heavy vehicles (PROCONVE-P) [20].

Figure 5 shows the evolution of the emission limits of CO, HC, NOx, and PM for HDV (Phases PROCONVE-P). As can be seen, the phases become increasingly restrictive. In phase P-1, HDV could emit a maximum of 14 g/km of CO, a value that decreased during the following phases, and in phase P-5 was 2.1 g/km, a reduction of approximately 85% in the emission of CO. Reduction of NOx started from 18 g/km in phase P-1 to 5 g/km in phase P-5 (reduction of 72%). The maximum emission of HC was 3.5 g/km in phase P-1, whereas in phase 5 this value decreased to 0.66 g/km, (reduction of 81%). Emissions of PM had regulatory limits, started only

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in phase P-2; in this phase, new HDV had to emit less than 0.6 g/km. This value decreased, and in the phase P-6, it was 0.02 g/km, which represents a reduction of 97% from the initial phase of PROCONVE for HDV.

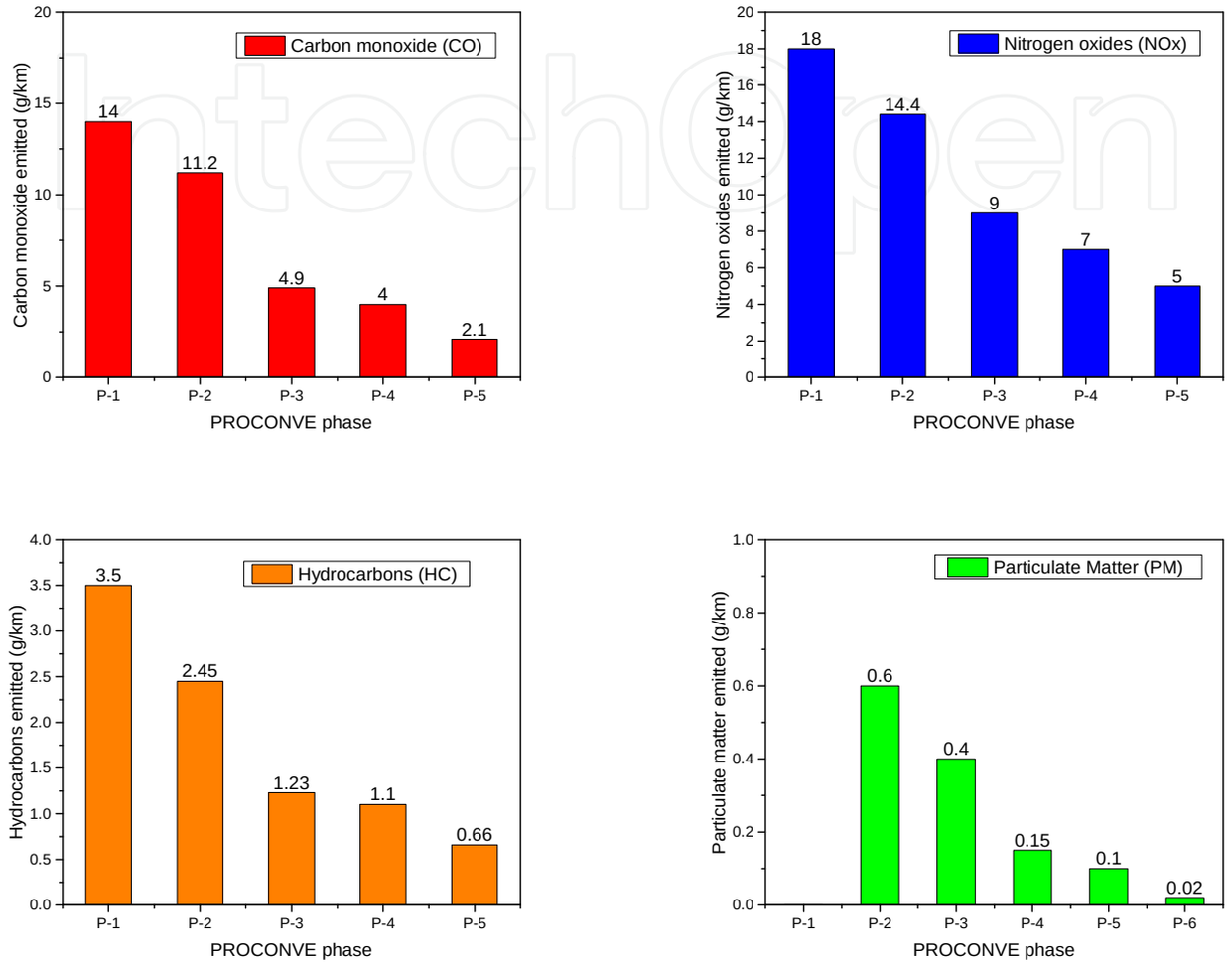

Figure 5. Evolution of the emission limits of CO, NOx, HC, and PM for HDV during the phases of PROCONVE-P.

Although established by the CONAMA Resolution 315/2002 [20], P-6 phase was not implemented on time due to delays in the specification of fuel (diesel) to be sold in Brazil. This fact caused delays in production of diesel with lower sulfur content and delays on the production of technological innovation engines of new vehicles. Reductions in the concentration of sulfur in diesel constituted a precondition for meeting the limits in P-6 phase, since the formation of sulfur compounds in combustion contributes to the so-called "poisoning" of the catalyst, not providing good operation, even in reducing emissions of NOx and HC.

In 2005, diesel S-2000 (2000 ppm of sulfur as a maximum limit) started to be sold in Brazil while S-500 (500 ppm of sulfur content in diesel) started to be sold only in the metropolitan areas. Reducing sulfur content in diesel from 13,000 ppm to 500 ppm provided a significant reduction of sulfur emissions in recent years. According to Resolution 315/2002 [20], which was not attended on schedule, after January 1, 2009, the P-6 phase should have started with S-500 diesel

been distributed in Brazil and diesel S-50 in metropolitan areas. However, this phase was not implemented on schedule, so CONAMA established in November 2008, through Resolution No. 403 [20], a new phase (P-7) for HDV, which has stricter emission limits. Low sulfur content fuel legislation is being established in Brazil as a result of new legislation (P-7), which requires exhaust gas recirculation (EGR) or selective catalytic reduction (SCR) aftertreatment systems implementation in new HDV, starting in January 1, 2012, which is equivalent to meet the Euro V European emission standards for heavy-duty diesel engines. This phase (P-7), started on January 1, 2012, and enabled the availability and commercialization of a diesel fuel with content of 10 ppm sulfur (S-10). The automobile and fuel industries are required until 2016 to adapt to new technical standards, providing diesel engines and fuels to Brazilian markets following patterns already adopted in Europe, where diesel vehicles emit sulfur content up to 200 times smaller than is released by the Brazilian buses and trucks.

3.3. Emissions of gaseous pollutants from vehicles in Brazil

The effects of adding different blends of hydrous ethanol to a reference gasoline on flex fuel engine was evaluated in a study developed by de Melo et al. [31]. The results showed that, in general, CO emissions were reduced with hydrous ethanol addition due to the higher oxygen content of the ethanol contributing to oxidation into CO_2. Total hydrocarbons emissions were also reduced, while aldehydes and unburned ethanol increased with hydrous ethanol addition. Emissions of NOx presented a complex behavior, without a particular defined trend. At 3875 rpm, knocking occurrence limited spark timing advance leading to lower NOx emissions when using gasoline E25 (without hydrous addition) and fuel blend content of 30% hydrous ethanol. With hydrous ethanol addition, there was a trend of NOx reduction at lower speeds (1500 and 2250 rpm), while for high speed (4500 rpm), there was a trend of NOx increase.

A comparative study was carried out of pollutant emissions produced by a mid-size sedan powered by 1.4-L spark ignition engine on a chassis dynamometer operating with three different fuels. Commercial gasoline with 22% of ethanol (E22, gasohol), compressed natural gas (CNG), and hydrous ethanol showed that in the cold start tests the E22 produced the lowest CO and HC emissions, while CNG produced the lowest NOx emissions [32]. Considering the full test cycle, CNG emitted the lowest CO, NOx, and CO_2 concentrations, and the lowest fuel consumption. Gasohol (E22) presented the lowest emission levels of HC and CH_4. Hydrous ethanol showed the highest fuel consumption and higher pollutant emission levels than the other fuels, except for CO_2, which was higher than CNG and lower than gasohol.

Randazzo et al. [33] investigated the effects of use of diesel/biodiesel blends with concentrations of 3% (B3), 5% (B5), 10% (B10), and 20% (B20) on a passenger vehicle exhaust emissions, and the results showed that increasing biodiesel concentration in the fuel blend increases CO_2 and NOx emissions, while CO, HC, and PM emissions were reduced. Additionally, the work evaluated the effects of anhydrous ethanol as an additive to B20 fuel blend with concentrations of 2% (B20E2) and 5% (B20E5). The results showed that the addition of anhydrous ethanol to B20 fuel blend can be a strategy to control NOx exhaust. However, the authors

concluded that it may require fuel injection modifications, since in this condition increases in CO, HC, and PM emissions were observed.

Pérez-Martinez et al. [34] showed that emissions factors for on-road LDV in the MASP in 2011 were 5.8 and 0.3 g/km, for CO and NOx, respectively. The values estimated in this study showed a significant reduction when comparing the values of emissions factors calculated in the experiment conducted in 2004 [35]. The values estimated in 2004 were 14.6 and 1.6 g/km, for CO and NOx, respectively. The reduction ratio was 2.5 times for CO and 3.2 for NOx. The authors attributed this fact to increased use of modern three-way catalysts using platinum and rhodium surfaces, which changes the nitrogen oxides back to nitrogen and elemental oxygen and complete the oxidation of CO to CO_2 [36]. In addition, there was the increased number of vehicles able to burn ethanol. In 2011, from the cars running in the MASP, about 55 % gasohol, 4 % burned hydrous ethanol, and 38 % were capable of burning both gasohol and hydrous ethanol (flex-fuel vehicles), while in 2004 about 69.5% of vehicles burned gasohol and 14.5% of the fleet burned hydrous ethanol. Regarding HDV, in 2011 the emissions factors estimated by Pérez-Martinez et al. [34] were 3.6 and 9.2 g/km, for CO and NOx, respectively, which represents a reduction of 5.7 and 2.4, for CO and NOx, in comparison with the data obtained for HDV running in 2004 in the MASP. In 2011, HDV burned a mixture containing 5% biodiesel, which may contributed to reduction in CO emissions [37], while minor decrease in emissions of NOx pollutant reported in the study may be associated with the use of biodiesel.

Guarieiro et al. [38] evaluated the exhaust emissions of a diesel engine running on biodiesel and operated by a steady-state dynamometer which provided a composition profile of the carbonyl compound emissions from exhaust of pure diesel (B0), pure biodiesel (B100), and biodiesel-diesel mixtures (B2, B5, B10, B20, B50, B75). This work showed that the mean concentration sum of total carbonyl compounds emission were 20.5 ppmv for B0 and 15.7 ppmv for B100, while for fuel blends the total concentration of carbonyl compounds were 21.4, 22.5, 20.4, 14.2, 11.4, and 14.7 ppmv, respectively, for B2, B5, B10, B20, B50, and B75. The study showed that major contributors to the total carbonyl compounds were formaldehyde and acetaldehyde, and that except for formaldehyde and acrolein, all carbonyl compounds showed a clear trend of reduction in the emissions from B2 to B100 (40% reduction, on average). The lowest total carbonyl emission factors were found when B50 was used, 2271 pg/g of fuel burned, while the individual emission factors determined (pg/g of fuel burned) were 539.7 (formaldehyde), 1411 (acetaldehyde), 30.83 (acrolein), and 310.7 (propionaldehyde).

Carbonyl compounds were measured in vapor-phase samples in a study developed in a Bus Station impacted by HDV fuelled with diesel/biodiesel fuel blend (B5) in Salvador, Bahia, Brazil, in 2012 [39]. Among them, formaldehyde, acetaldehyde, and propanone were the major quantified compounds, ranging from 28.4 to 287.3 ppbv (formaldehyde), 24.9 to 171.3 ppbv (acetaldehyde), and 5.8 to 72.3 (propanone). The data obtained in this site were compared to formaldehyde and acetaldehyde concentrations found in other sites impacted by HDV fuelled with pure diesel and diesel/biodiesel blends. The authors reported that the addition of concentrations higher than 3% of biodiesel to diesel showed an improvement in the carbonyl concentration profile at these places with high flow of HDV, and that the use of these biofuels revealed profiles similar to those found for sites less impacted by

these vehicles. Higher concentrations of these carbonyls were observed in the current study compared to the results obtained in the same bus station in 1997 [40]. The average formaldehyde and acetaldehyde concentrations increased approximately 1.5 and 7 times, respectively, between the two observation periods. The authors suggested that these significant differences found between the two sampling periods can be explained by the increase of the vehicle fleet currently circulating in the Lapa Bus Station. While in 1997 the vehicular fleet at the Lapa bus station was 150 buses per hour, in 2010 it was over 330 buses per hour. In this manner, an increase of the vehicle fleet circulating in Lapa station can reflect a rise of both formaldehyde and acetaldehyde emission concentrations at that site. Other factors suggested by the authors was that the reason for the observed increase of carbonyl compounds concentration at this site was related to changes of the fuels used in vehicles. In 1997, buses were fuelled with pure diesel and in 2012 they were fuelled with B5 fuel blend. The results of an experimental campaign at a central bus station in Londrina, Brazil, where only pure diesel powered vehicles circulated showed that the formaldehyde concentrations were significantly higher than acetaldehyde [41]. The formaldehyde levels ranged from 6.17 to 10.43 ppbv with an average of 7.94 ppbv, while acetaldehyde presented levels in the interval of 0.49 to 2.12 ppbv with an average of 1.26 ppbv. The formaldehyde concentration was six times higher than the acetaldehyde concentration.

Nogueira et al. [42] determined on-road emissions of carbonyls from Brazil's current vehicle fleet based on two experimental campaigns conducted in traffic tunnels located in the MASP. Among carbonyl species, formaldehyde and acetaldehyde were the most abundant compounds found during all sampling time intervals. The higher carbonyl emissions were associated with HDV, which were fueled with a blend of regular diesel and 5% biodiesel from soy. LDV were responsible for high emissions of acetaldehyde, since in Brazil this type of vehicle burns a mixture of 75% (v/v) gasoline and 25% ethanol (gasohol), or hydrous ethanol. Brazilian LDVs reported emission of 5.7 mg/km and 7.4 mg/km for formaldehyde and acetaldehyde, respectively. When compared with data from LDV in the California, these values are 352% and 263% higher than that emitted by vehicles running on E10 (gasoline with 10% ethanol). The HDV average emission factor for formaldehyde and acetaldehyde was 28 and 20 mg/km, respectively, indicating that there was a reduction in the HDV emission of formaldehyde (42%) and acetaldehyde (58%) when comparing with the values obtained in an experiment conducted in the MASP in 2004 [35]. HDV running in 2011 in the MASP with diesel + 5% biodiesel showed formaldehyde emissions 33% higher than HDV running in California in 2010 with regular diesel [43].

Figure 6 shows the aldehyde emissions in milligrams per kilometer traveled by new vehicles sold in Brazil, together with the limits specified in each phase of the PROCONVE. As it can be seen, significant reductions in emissions occurred due to the evolution of pollution control public policies. Prior to 1992 (before and during phase 1 of the PROCONVE), no limits existed regarding aldehyde emissions. During that period, vehicles running on ethanol emitted about 0.13 g of total aldehyde (RCHO) per kilometer, about three times higher than vehicles running on gasohol. In phase 2 of the PROCONVE, which started in 1992, when the emission limit was initially 0.15 g of aldehyde per km traveled but later reduced to 0.03 g of aldehyde per km

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traveled by 1997 (the beginning of Phase 3). As observed, vehicles running on ethanol emit more total aldehydes than do vehicles running on gasohol and the quantity of aldehydes emitted by ethanol-powered vehicles is similar to that emitted by flex-fuel vehicles running on ethanol. However, the production of vehicles powered by ethanol only was discontinued in 2006, and there are therefore no longer any records of emissions for new vehicles. It is also noteworthy that flex-fuel vehicles manufactured in 2010 emitted an average of 0.007 g of aldehyde per km when new and using ethanol, which was about 65% less than their 2003 counterparts under the same conditions. The PROCONVE is currently in phase 6, and the limit for aldehyde emissions is 0.02 g per km traveled.

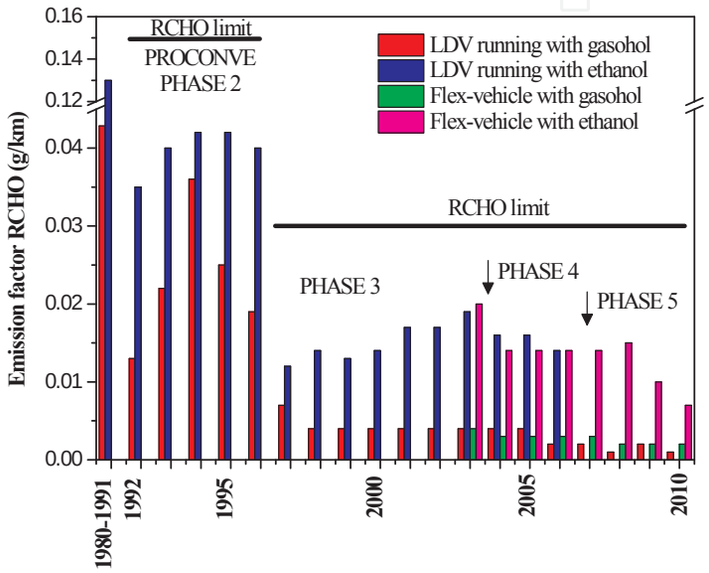

Figure 6. Total aldehydes (RCHO) emission factors from 1980 to 2010 for Brazilian LDV running with gasohol and ethanol fuels, and the phases of the PROCONVE.

3.4. Emissions of particulate matter from vehicles in Brazil

Atmospheric aerosol or particulate matter (PM) is a complex mixture of extremely small particles and liquid droplets, presenting also a complex chemical composition [44, 45]. The atmospheric PM is a stable suspension of liquid or solid particles with an aerodynamic diameter lower than 100 μm. Actually, the classification of PM size is very important due to its effects on human health and/or its direct and indirect effects in the environment and climate. The concentrations, size, and number distributions of particles are affected by physical and chemical processes or kinds of sources (natural or anthropogenic, and secondary atmospheric aerosol production). The inhalable particles have aerodynamic diameter equal or lower than 10 μm (PM_{10}), being divided into fine ($PM_{2.5}$) and coarse ($PM_{2.5\text{-}10}$) particles [44, 45]. It is important to emphasize that to control both the PM emissions by burning fuels and air quality, the legislation considers the mass concentration (μg/m^3) for a given particle size range ($PM_{2.5}$ and PM_{10}), without any relationship with the chemical composition. This parameter is valid for the national air quality standards, and also for the WHO guidelines [46]. For PM, even

though the mass concentration, the most important parameter in legislation, the chemical composition measurements can contribute to better knowledge not only to the emission processes but also to the effects on health and environment. The PM is a complex mix of different elements and compounds both inorganic and organic/carbonaceous, which includes the ions (sulfate, nitrate, chloride, ammonium, sodium, potassium, calcium, and magnesium), the trace elements and/or metals (Pb, Zn, Ni, Cu, V, Cr, Cd, Al, P, S, Si, Ti, Ca, Fe, and others), elemental carbon (and black carbon) and organic compounds from simple hydrocarbons to oxygenated, aromatics, and polycyclic aromatic hydrocarbons. The fraction of these different compounds in the PM mass is due to sources and/or of the physical-chemical processes during the particles' life cycles [44, 45]. The heavy metals in the form of free elements are non-toxic. However, they are dangerous in their cationic form and when bound to short carbon chains. The metal ions form complexes with a large amount of binders and influence the biological functions, affecting the normal development of living beings' tissues and their adequate functioning [47]. Heavy metals, also referred to as trace elements, are an important fraction of the PM because they represent a risk to human health. Trace metals in airborne PM were considered to represent a health hazard since they can be absorbed into human lung tissues during breathing. Although many of these metals are constituents of tissues, their toxic effects are known even at low levels. Inorganic ions, as well as other PM constituents, result from fuel burning. In addition, these pollutants affect climate change, contribute to the acidification of aerosol, changing its conductivity [48]. Therefore, it is extremely important to have a qualitative and quantitative understanding of the PM composition and the contribution of fuel burning as well as the role of biofuel addition.

The speciation of organic compounds is still a major challenge, being an important advancement the differentiation between organic carbon and elemental carbon (or graphitic). Special attention is necessary for black carbon (BC) and elemental carbon (EC) measurements and reports [49]. BC is an important component of the PM, produced by incomplete combustion processes (fossil fuels, biofuels, and biomass), having a graphite-like microstructure, being strongly absorbent of visible light, refractory and insoluble in water and in organic solvents including methanol and acetone [49]. As BC is the most strongly light absorbing component of PM, it absorbs both incoming and outgoing radiation of all wavelengths, which contributes to warming of the atmosphere and darkening of the surface. It is, therefore, a pollutant that has important climatic influences [50].

One of the most important groups of organic compounds is the polycyclic aromatic hydrocarbons (PAH) that are present in the gas- and particle-phase in ambient air as well as other environmental compartments. These organic compounds have known mutagenic and carcinogenic properties. Due to this harmful effect of some PAH to humans, the US EPA shows them in its priority pollutants list, being some PAH structures shown in Figure 7. The lipophilicity, environmental persistence, and genotoxicity increase with heavier molecular weight from 4 to 6 aromatic rings [51-54]. PAHs are formed by the pyrolysis and incomplete combustion of organic compounds [55, 56]. A major source of this class of pollutants in large urbanized centers is the vehicular emission. Fuel burning produces, among other pollutants, measurable concentrations of PAH, depending on the characteristics of the fuel.

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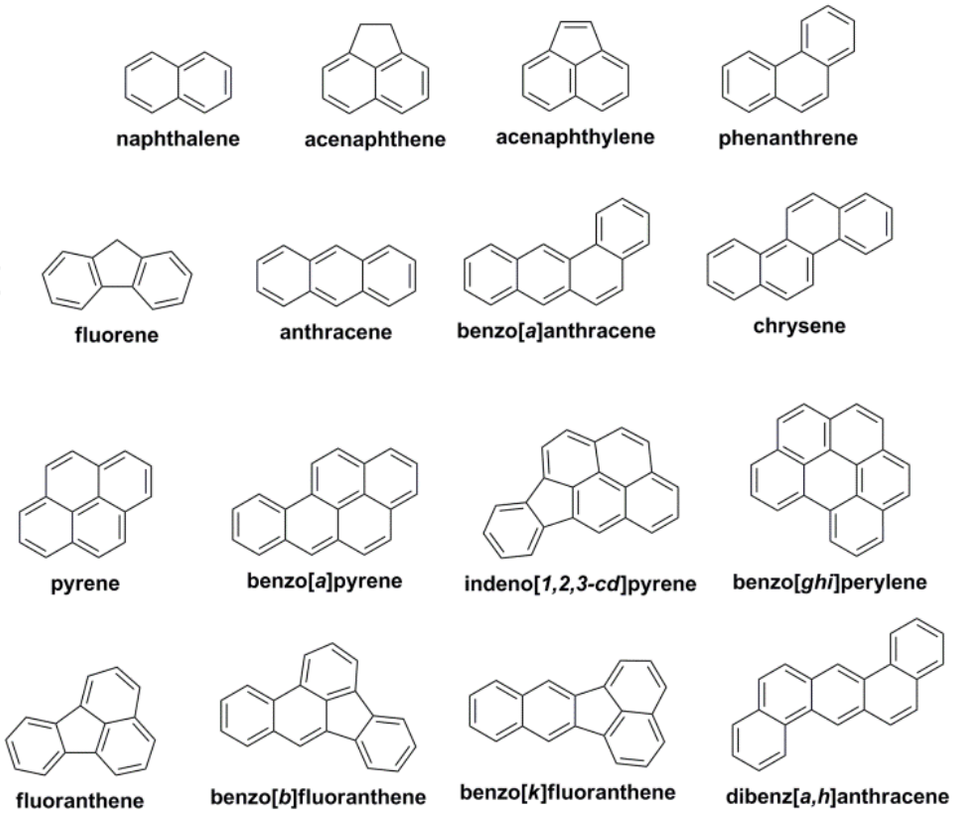

Figure 7. Structures and nomenclatures of the 16 PAHs on the EPA priority pollutant list.

The analytical techniques used for determination and quantification of the PM components, not only for emissions but also for atmospheric measurements, are shown in Table 3. These techniques include continuous aerosol sampling and analysis systems or analysis methods that are commonly applied to aerosol filter samples. The details of the analytical methods, advantages, and disadvantages are available in an important review about PM sampling and measurements [57]. Another important discussion involves the question of the appropriateness of sampling and analysis methods of PM for the purpose of adapting the requirements needed to establish emission and air quality standards. This discussion involves size-selective inlets (cyclonic flow, impactor, virtual impactor, and selective filtration), if the sampling is continuous or integrated in time (24 h standard), filters characteristics for only mass quantification or also for chemical composition (membranes of Teflon, polycarbonate, glass fiber, cellulose esters, or silver), plus the details regarding the flow measurement, flow control, and flow movers [58]. In the past decades, new techniques development enabled measurements of aerosol integral properties (total number concentration, cloud condensation nucleus concentration, optical coefficients, etc.), aerosol physical chemical properties (density, refractive index, equilibrium water content, etc.), measurements of aerosol size distributions, and measurements of size-resolved aerosol composition [59].

Emission quantifications (mass per kilometer traveled or mass per fuel mass burned) are calculated based on dynamometers (vehicles or motors) or tunnels experiments, being that the former corresponds an individual emission, while the latter represents the real fleet. Evalua-

tion of influence of direct emissions on air pollutants concentrations from fuel burning by vehicles can be happened by experiments in special sites, like bus stations, close streets or avenues with heavy traffic, etc.

Constituents of PM	Usual analytical techniques
Mass	Gravimetric (filter weighing); beta attenuation monitor (BAM); tapered element oscillation microbalance (TEOM); quartz crystal microbalance (QCM)
Black carbon	Optical reflectometer (also called spotmeter and filter smokemeter); aethalometer; multi-angle absorption photometer (MAAP); photoacoustic soot sensor (PASS)
Total carbon: organic vs. elemental (graphitic)	Thermal/optical reflectance (TOR) or thermal/optical transmittance (TOT)
Elements and/or metals (Pb, Zn, Ni, Cu, V, Cr, Cd, Al, P, S, Si, Ti, Ca, Fe, Mg, Mn, K, As, Sb, Se, Co, In, Eu)	X-ray fluorescence analysis (XRF); particle induced X-ray emission (PIXE); atomic absorption spectrometry (AA); emission spectrometry (EE); inductively coupled plasma-mass spectroscopy (ICP-MS); instrumental neutron activation analysis (INAA) anodic stripping voltammetry (ASV)
Inorganic ions (Cl., NO_3^-, SO_42^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+) and/or carboxylate anions	Ionic chromatography (IC)
Speciation of organics	Solvent extraction by Soxhlet techniques / cleanup by solid-phase extraction (SPE) follow analysis by high-performance liquid chromatography (HPLC) with various detectors (absorption, fluorescence, and mass spectrometry) / gas chromatography flame ionization detector (CGFID) / gas chromatography mass spectrometry (CGMS)

Table 3. Some analytical techniques for analysis of the main constituents of particle matter.

Tunnel experiments were performed in MASP in different times and even sampling in two tunnels, one with predominance of light-duty vehicles (LDV) that burn gasohol (75% gasoline + 25% anhydrous ethanol) and ethanol, and one that had LDV plus significant number of heavy-duty vehicles (HDV) that burn diesel and/or diesel + biodiesel [60]. Experiments during 2011 showed that LDV and HDV running in the Metropolitan Area of São Paulo has emitted less $PM_{2.5}$ in recent years than in the past [34]. In 2004 [60], LDV emitted 92 mg of particles ($PM_{2.5}$) per kilometer traveled, while in 2011 [34] this value decreased to 20 mg/km, a reduction of 4.6 times. Emissions from HDV decreased from 588 mg/km in 2004 to 277 mg/km in 2011, a reduction about 2 times. These data showed that LDV have a greater reduction in PM emissions, since in this period of study there was an improvement in the engine technology of LDV. Furthermore, in this period there was the introduction of flex fuel vehicles, and consequently the consumption of ethanol by vehicles has increase. On the other hand, HDV showed no major advances in engine technology, occurred only improves in the composition

of diesel oil, for example, a reduction in sulfur content, and the addition of biodiesel to diesel (in 2011 vehicles circulated with 5% biodiesel).

Guarieiro et al. [61] evaluated the emission effects of biodiesel addition of 4% of soy biodiesel (B4), a biodiesel blend of 25% and 50% (B25 and B50) in diesel, and also pure biodiesel (B100). In this study, PM emissions were measured on a steady-state dynamometer in a test using a diesel engine at low load. Size-fractionated PM samples were collected using the NanoMOUDI impactor and analyzed for the 16 priority PAHs. In addition, $PM_{2.5}$ samples were collected and analyzed for redox activity by DTT assay. PM was distributed in all sizes, while PAH size distributions were found at higher levels in the accumulation mode (30 nm < Dp < 2.5 μm). Total PAH emission factors for B4, B25, B50, and B100 were 237, 111, 182, and 319 ng/kg fuel burned, respectively. Individual PAH emission factors showed that PAH containing four or more rings (MW > 202) such as benzo(b)fluoranthene, benzo(a)anthracene, pyrene, and benzo[ghi]perilene were the main PAH emitted by the four studied fuels. The study showed that percentage reductions of individual PAH emission factors for the blend fuels in comparison with B4 were 37% and 22% for B25 and B50, respectively, and an increase around 31% for B100. This work also showed an increase in redox activity for B25, B50, and B100 when compared to B4. The results from this study suggest that emissions from pure waste cooking biodiesel may not be the better fuel choice in terms of PM, PAH, BaPE (corresponding carcinogenicity index) particle size distribution and emission factors as well as redox activity. However, B25 and B50 blends presented some improvements in terms of PM, PAH, BaPE size distribution, and redox activity of engine exhaust in comparison to B4. The results suggest that addition of low percentages biodiesel to diesel promotes benefits in both environmental and human health concerns [61].

Exhaust emissions of 17 polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) were compared from LDV fueled with gasohol and fueled with hydrous ethanol [62]. In this study were evaluated the influence of fuel type and quality, lubricant oil type, and use of fuel additives on the formation of these compounds. The results showed that emission factors of PCDD/Fs for the gasohol vehicle varied from undetected values to 0.068 pg international toxic equivalency/km traveled, whereas in the ethanol vehicle the observed variation ranged between 0.004 to 0.157 pg international toxic equivalency/km. The study also showed that use of fuel additive significantly diminished the emission of octachlorodibenzo-p-dioxin, in the gasohol-powered vehicle, whereas in the ethanol vehicle no significant associations were observed between the investigated variables and the emissions. The results of another study showed that vehicles running on gasohol emitted more of total PAH; the emission factors varied from 41.9 μg/km to 612 μg/km than vehicles running on ethanol from 11.7 μg/km to 27.4 μg/km [63]. The authors reported that in terms of benzo(a)pyrene toxicity equivalence, emission factors varied from 0.00984 μg TEQ/km to 4.61 μg TEQ/km for the gasohol vehicle and from 0.0117 μg TEQ/km to 0.0218 μg TEQ/km in the ethanol vehicle. The results also showed that the use of fuel additive for the gasohol vehicles cause a significant increase in the emission of naphthalene and phenanthrene, while the use of synthetic oil, instead of mineral oil, also contributed significantly to a decrease in the emission of naphthalene and fluorene. Regarding hydrous ethanol-powered vehicle, the same compounds were

tested and showed no statistically significant influence on PAH emissions. Emissions of PAH from LDV running with ethanol or gasohol are lower than vehicles running with diesel, being that the diesel-powered vehicles showed emission about 200 times higher than vehicles running with ethanol [64]. Total PAH values from diesels ranged from 1.133 to 5.801 mg/km. Naphthalene, phenanthrene, fluoranthene, pyrene, and chrysene were detected in all test samples. Another study developed by da Silva et al. [65] evaluated the composition of inhalable particles and their trace metal content in LDV fueled with ethanol and gasohol. The results showed that the total emission factors ranged from 2.5 to 11.8 mg/km in the gasohol vehicle, and from 1.2 to 3 mg/km in the ethanol vehicle. The majority of particles emitted were in the fine fraction ($PM_{2.5}$), in which Al, Si, Ca, and Fe corresponded to 80% of the total weight. The results also showed that PM_{10} emissions from the ethanol vehicle were about threefold lower than those of gasohol.

Correa and Arbilla [66] evaluated the emissions of mono- and polycyclic aromatic hydrocarbons (MAHs and PAHs, respectively) from a six cylinder heavy-duty engine, typical of the urban buses of Brazilian fleet, fueled with pure diesel (D) and biodiesel blends (v/v) of 2% (B2), 5% (B5), and 20% (B20). The results showed the following average reduction of MAHs: 4.2% for B2 blend, 8.2% for B5 blend, and 21.1% for B20 blend. The average reductions for PAHs were 2.7% (B2), 6.3% (B5), and 17.2% (B20). However, some PAHs and MAHs emissions increased due to the biodiesel blends like phenanthrene, ethyl benzene, and trimethyl benzenes.

In order to characterize current concentrations of $PM_{2.5}$ from LDV and HDV in the MASP, Brazil, measurements of physical and chemical properties of aerosol were undertaken inside two tunnels located in the MASP in 2011 [67]. The two tunnels showed very distinct fleet profiles: in the Janio Quadros (JQ) tunnel, the vast majority of the circulating fleet are LDV, fuelled on average with the same amount of ethanol as gasoline. In the Rodoanel tunnel (RA), PM emission is dominated by HDV fuelled with diesel + 5% biodiesel blend. The study shows that in the JQ tunnel, $PM_{2.5}$ concentrations were on average, 52 $\mu g/m^3$, with the largest contribution from organic mass (42 %), followed by elemental carbon (17 %) and crustal elements (13 %). While in the RA tunnel, $PM_{2.5}$ was on average 233 $\mu g/m^3$, mostly composed of elemental carbon (52 %) and organic mass (39 %). The work showed that average organic mass:elemental carbon ratio in the JQ tunnel was 1.59, indicating an important contribution of elemental carbon despite the high ethanol fraction in the fuel composition. The study also shows that the sum of the PAHs concentration was 56 ± 5 ng/m^3 and 45 ± 9 ng/m^3 in the RA and JQ tunnel, respectively. In the JQ tunnel, benzo(a) pyrene (BaP) ranged from 0.9 to 6.7 ng/m^3 (0.02-0. 1 parts per thousand of $PM_{2.5}$) whereas in the RA tunnel BaP ranged from 0.9 to 4.9 ng/m^3 (0.004-0.02 parts per thousand of $PM_{2.5}$), indicating an important relative contribution of LDV emission to environmental BaP concentration.

The concentrations of $PM_{2.5}$ and PM_{10}, including their ionic composition was evaluable at an underground bus terminal, being that buses burning fuel blend of 95% diesel + 5% biodiesel (B5) in Salvador, Bahia, Brazil, in 2010 [68]. The results showed that the mean mass concentrations of $PM_{2.5}$ were 201 $\mu g/m^3$ during the daytime (8 am-7 pm), while the PM_{10} were 309 $\mu g/m^3$, during the same period of the day. Three times lower PM_{10} concentration (110 $\mu g/m^3$) was

obtained from an experiment conducted at the same place in 2005, before addition of biodiesel to diesel [69]. The mean concentrations for the total carboxylate anions during the day were 139 and 180 ng/m^3 for $PM_{2.5}$ and PM_{10}, respectively. Results showed that monocarboxylate anions (propionate, acetate, and formate) were the most abundant, followed by ketocarboxylate anions (pyruvate), while the dicarboxylate anions (oxalate and malonate) were the least abundant. The ion Mg^{2+} (0.43 μg/m^3) was the most important cation and NO_3^- (0.083 μg/m^3) the main anionic species in $PM_{2.5}$, while Na^+ (0.60 μg/m^3) and SO_4^{2-} (0.62 μg/m^3) were the most abundant in [68].

The PM_{10} concentration (24 h) varied from 38.8 to 92.2 μg/m^3 on a bus station, for buses running with diesel/biodiesel fuel blend (B3) in the city of Londrina, Paraná, Brazil, during July 2008 [70]. Nitrate (8 μg/m^3), sulfate (1.4 μg/m^3), and ammonium (0.3 μg/m^3) presented the highest concentration levels, suggesting that biodiesel may also be a significant source for these ions, especially nitrate. The authors also demonstrate that a higher fraction of PAH particles was found in particles with diameters smaller than 0.25 μm in the Londrina bus station, and that the fine and ultrafine particles were dominant among the PM evaluated, suggesting that biodiesel decreases the total PAH emission. However, the authors suggested that use of biodiesel increased the fraction of fine and ultrafine particles when compared to diesel emissions by heavy-duty vehicles obtained in a 2002 campaign [71].

4. Vehicular emissions and the impacts on air quality

Vehicular emissions contain lead to a generation of various toxic substances such as carbon monoxide (CO), nitrogen oxides (NOx = NO + NO_2), hydrocarbons (HC), sulfur oxides (SOx), and particulate matter (PM) which, when in contact with the respiratory system, can produce several harmful health effects. The effects are related to respiratory diseases, increased incidence of cancer, cardiovascular diseases, neurological problems, and reproductive problems [72]. Biofuels have met a niche in the growing market as a consequence of economic policies (substitution of fossil fuels) or efforts to reduce air pollution caused by vehicular emissions. In Brazil, the CONAMA Resolution Nº 3 by 28/06/1990 determines the standards for air quality and suitable measurement methods. This resolution establishes standards for PM, smoke, inhalable PM, SO_2, CO, O_3, NO_2, and several sampling methods and analysis of pollutants. Table 4 shows the maximum and the desirable levels of standard concentration of air pollutants, which aims to protect people's health and the environment.

Despite the guidelines of the World Health Organization [46] for PM_{10} and $PM_{2.5}$, there is only national air quality standard for PM_{10} in Brazil (Table 4), being the Brazilian values higher than the WHO guidelines (50 μg/m^3 24 h mean and 20 μg/m^3 annual arithmetic mean for PM_{10}; and 25 μg/m^3 24 h mean and 10 μg/m^3 annual arithmetic mean for $PM_{2.5}$). The monitoring of air quality in Brazil is the responsibility of the States. However, few states have established air quality network, and only eight metropolitan areas (States' capitals) have been continuously monitored: Distrito Federal, Vitória, Belo Horizonte, Rio de Janeiro, São Paulo, Porto Alegre, Curitiba, and Salvador. In Rio de Janeiro and São Paulo States, other cities have also been monitored [73].

Pollutant	Averaging Time	Maximum Level (μg/m³)	Desirable Level (μg/m³)	Method of measuring
Total suspendend Particles	24 hours	240	150	High volume air sample / gravimetric
	Annual geometric	80	60	
Inhalable particles	24 hours	150	150	Gravimetric / inertial separation
	Annual arithmetic	50	50	
Smoke	24 hours	150	100	Reflectance
	Annual arithmetic	60	40	
SO_2	24 hours	365	100	Fluorescence pulse / pararosaniline method / ion chromatography
	Annual arithmetic	80	40	
NO_2	1 hour	320	190	Chemiluminescence
	Annual arithmetic	100	100	
CO	1 hour	40.000	40.000	Nondispersive infrared sensor
	8 hours	10.000	10.000	
O_3	1 hours	160	160	Ultraviolet

Table 4. National standards for air quality [99].

Thus, MASP quality monitoring data are more complete (in time and space), enabling the evaluation of air quality trends as a result of actions to control pollutants emissions. Almost 30 years after the creation of PROCONVE, results show that the implemented strategy is correct, and the adoption of increasingly restrictive phases was successful. As observed in Figure 8, atmospheric concentration data show a clear downward tendency for CO, a recognized pollutant emitted from incomplete fuel combustion, in the MASP over the past years. These data show that LDVs emitted 20 g/km on average in the 1980s and 0.3 g/km in 2010. Meanwhile, CO concentrations recorded in CETESB monitoring network reached values close to 30 ppmv. On the other hand, since 2008, the air-quality standards for 8-hour carbon monoxide (9 ppmv) have not been exceeded at any of the automatic monitoring stations in the MASP. In agreement, analysis about the trends of air quality in the MASP showed that although the fleet had increased at a substantial rate, annual mean values showed that all pollutants except for ozone have been decreasing in the latest years [74], as a result of the vehicular emission control program established by PROCONVE. The trend evaluation of all monitoring stations showed a decrease in the annual mean concentration levels of CO, NOx, PM_{10}, and SO_2, being on average -0.09 ppm/year, -1.82 μg/m³/year, -1.97 μg/m³/year, and -0.82 μg/m³/year, respectively [74].

An important analysis about air quality studies in MASP reported that atmospheric concentrations of acetaldehyde and ethanol were higher in Brazil than in other areas of the world,

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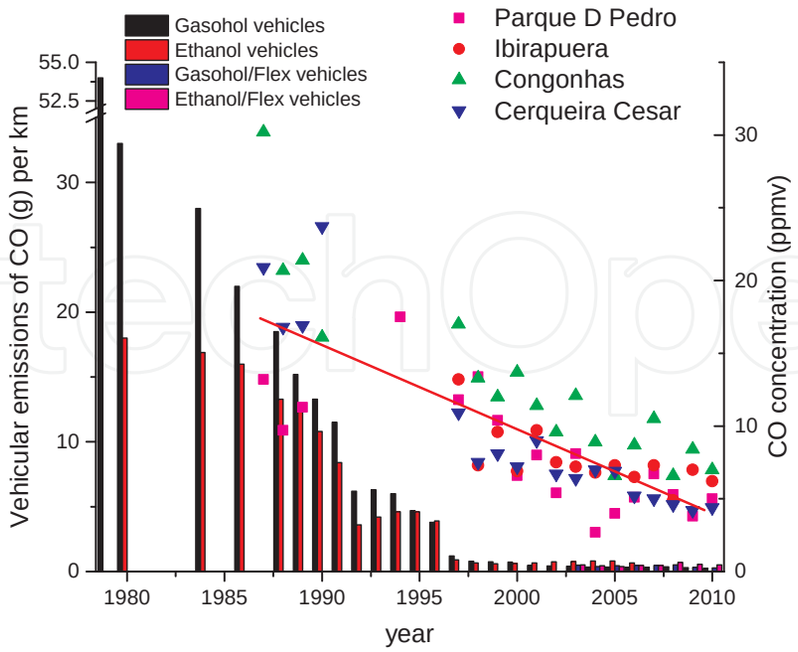

Figure 8. Carbon monoxide (CO) emissions from LDV by type of fuel and CO environmental concentrations (annual average) recorded by CETESB at automatic monitoring stations Parque Dom Pedro, Ibirapuera, Congonhas, and Cerqueira Cesar.

whereas the concentrations of aromatic compounds and carboxylic acids were lower [75]. More recent results analyzed atmospheric concentrations of ozone, nitrogen oxides (NO and NO_2), formaldehyde, and acetaldehyde measured in the MASP, over four seasons in 2012 and 2013 [76]. These results demonstrated that although there was a large increase in the number of vehicles in the MASP that use ethanol ("flex-fuel" vehicles), technological advances in vehicle emissions control have prevented any significant increase in the atmospheric concentrations of aldehydes. The average concentrations of formaldehyde and acetaldehyde were 8.6 ± 6.7 ppbv and 5.4 ± 5.2 ppbv, respectively. Both carbonyls are important constituents of the urban troposphere in the MASP (third and fourth in terms of concentration), representing an important fraction of the total VOCs.

In recent years, Brazilian LDVs have shown a reduction in aldehyde emissions. During the 1980s, most Brazilian vehicles did not use catalytic systems for the conversion of exhaust gases and the engines were less efficient. Since 2003, flex-fuel vehicles available on the Brazilian market have been equipped with modern three-way catalytic converters. Additionally, regulations in the PROCONVE program have been of great importance in reducing the emissions of pollutants (e.g., aldehydes) in the atmosphere. In the study developed by Martins et al. [77], the data also suggest a decrease of aldehydes concentration in the MASP between years 1986 and 2003. On the other hand, comparing to previous data, this study showed that the concentration of HC presented no decrease in the concentration. Among the HCs species analyzed, the highest concentrations observed were those of toluene (7.5 ± 3.4 ppbv), n-decane (3.2 ± 2.0 ppbv), benzene (2.7 ± 1.4 ppbv), and 1,3,5-trimethylbenzene (2.2 ± 1.5 ppbv) [77]. In some years, the highest formaldehyde values in Brazil have been recorded in the city of Rio

de Janeiro, where those values increased considerably between 1998 and 2004, whereas formaldehyde and acetaldehyde levels both decreased sharply between 2004 and 2009. In the latter period, values ranged from 1.52 to 54.3 ppbv for formaldehyde and from 2.36 to 45.6 ppbv for acetaldehyde [78, 79]. The authors attributed high aldehyde concentrations to the increasing use of biofuel. Several researchers have worked out the reaction pathways in the combustion of different biofuels and have concluded that such processes can generally be expected to produce carbonyl compounds, particularly formaldehyde [80, 81]. In a study developed in 2000 showed ambient concentrations of up to 61 carbonyls measured in Rio de Janeiro, Brazil. The most abundant carbonyls were formaldehyde and acetaldehyde (8.8 pbbv and 5.8, respectively) followed by acetone, 2-butanone, and benzaldehyde. Ambient concentrations of other carbonyls (except acetophenone) correlated well with those of acetaldehyde and formaldehyde [82].

The concentration of atmospheric VOCs in the MASP, such as alcohols and aldehydes, were measured and compared with the data obtained in Osaka, Japan [83]. The results showed that concentrations of several pollutants found in Brazil were higher than in Japan. Ethanol concentrations found in Sao Paulo were significantly higher than those in Osaka, where the average concentrations of atmospheric methanol, ethanol, and isopropanol were 5.8 ± 3.8, 8.2 ± 4.6, and 7.2 ± 5.9 ppbv, respectively, while the average ambient levels of methanol, ethanol, and isopropanol measured in Sao Paulo were 34.1 ± 9.2, 176.3. ± 38.1, and 44.2 ± 13.7 ppbv, respectively. The levels of aldehydes, which were expected to be high due to the use of alcohol fuel during this period, were also measured at these sampling sites and the atmospheric formaldehyde average concentration measured in Osaka was 1.9 ± 0.9 ppbv; the average acetaldehyde concentration was 1.5 ± 0.8 ppbv. The atmospheric formaldehyde and acetaldehyde average concentrations measured in Sao Paulo were 5.0 ± 2.8 and 5.4 ± 2.8 ppbv, respectively. The ethanol/methanol and acetaldehyde/formaldehyde were compared between the two measurement sites and elsewhere in the world, which have already been reported in the literature. Due to the use of ethanol-fueled vehicles, these ratios, especially ethanol/methanol, are much higher in Brazil than those measured elsewhere in the world. Colon [84] compared environmental concentrations of some VOCs in the MASP with data obtained from EPA in Los Angeles. In their study, the overall MASP results demonstrated that the mean concentrations of single-ring aromatics are 2-3 times higher; volatile aldehydes are 5-10 times higher; and simple alcohols 10-100 times higher as compared to results of an EPA in the Los Angeles basin. In addition, n-alkanes containing between 4 and 11 carbons were only slightly elevated in Sao Paulo.

Particulate matter, main for PM_{10}, had more data about mass concentrations, due to States air quality monitoring stations, as well as studies by different research groups around the country. The first diagnosis of air quality monitoring network in Brazil showed the representation of differences both in space and in time. In the analysis for PM_{10} concentration, few stations had values above the national primary standard in 2012, but considering WHO guidelines the majority showed values above 20 reaching up to 100 $\mu g/m^3$, being that the higher values were observed in São Paulo and Rio de Janeiro, more populated urban areas in Brazil (IEMA, 2014).

In urban areas, such as the MASP, the fuel burning by vehicles is an important source of PM; when comparing current levels to those observed in the past, it appears that there has been an improvement in concentration levels of this pollutant, as result of the actions and emission control programs that took place over time. In recent years, the average concentrations tended to stabilize, indicating that even with diminishing vehicle emissions these levels are only sufficient to offset the increase in the fleet and the ensuing traffic conditions. Figure 9 shows the reduction on PM_{10} concentrations recorded in selected CETESB monitoring network. Since 2004, the value of Brazilian air quality standard (50 μg/m^3) for PM_{10} was not exceeded, but for all monitoring stations the annual mean values were above the WHO (20 μg/m^3) guidelines (Figure 9). Although there is no national air quality standard for $PM_{2.5}$, CETESB has monitored this pollutant; and since 1987 it corresponds to 60% of the PM_{10} mass in MASP atmosphere [28].

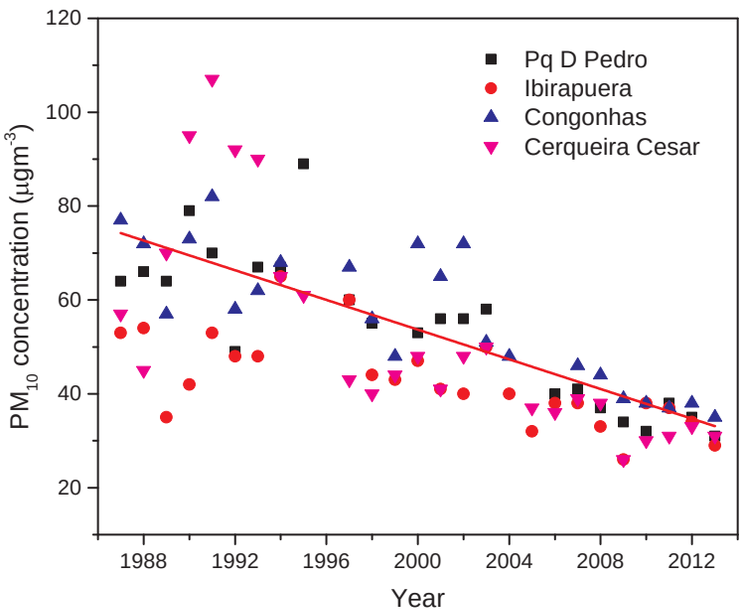

Figure 9. Annual arithmetic mean of MP_{10} concentrations recorded at CETESB automatic monitoring stations: Parque Dom Pedro, Ibirapuera, Congonhas, and Cerqueira Cesar, from 1987 to 2013.

Sampling and analysis of chemical composition of $PM_{2.5}$ were held for six Brazilian capitals (São Paulo, Rio de Janeiro, Belo Horizonte, Curitiba, Recife, and Porto Alegre) between 2007 and 2008 [85, 86], evaluating differences between summer and winter concentrations, meteorological influences, physicochemical profiles, and the effects on human health. The sources evaluation by receptor models identified the principal factors: soil and crustal material; vehicle emissions and biomass burning; and fuel oil combustion in industries (sulfur factor), being that vehicle emissions explained at least 40% of the $PM_{2.5}$ mass [86]. The concentrations of mass, black carbon (BC) and major ions in $PM_{2.5}$ are shown in Table 5, together with concentrations obtained in other places of Brazil, like as industrial site and region where sugar cane is routinely burned. The $PM_{2.5}$ mass concentrations were higher than the WHO guidelines, except in Recife. In urban areas, BC concentrations were higher than ions concentrations, being the sulfate

concentrations higher than those of any other ion. The lowest sodium concentrations were observed in Belo Horizonte and Curitiba, which are farther from the ocean, on the contrary those observed in Seropédica and Santa Cruz (Rio de Janeiro) [87], which are near the ocean (Table 5). São José dos Campos and Araraquara had the highest potassium contents, which were associated with the occurrence of biomass burning events (for instance, sugar cane). Regarding trace elements and/or metals (Table 6), iron concentration was the highest followed by aluminum and zinc. The $MP_{2.5}$ PAH results are shown in Table 7, highlighting the high concentrations of total PAHs observed in São Paulo and Cubatão, more polluted areas among the cities evaluated.

		Average Concentrations / μg m^{-3}										References
City/State	**Sampling data**	**Mass**	**BC**	**Cl^-**	**NO_3^-**	**SO_4^{2-}**	**NH_4^+**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	
Seropédica/Rio de Janeiro	Aug. 2010-July 2011	12.1	-	1.07	1.70	3.30	-	1.59	0.23	0.24	0.07	[87]
Santa Cruz/Rio de Janeiro		12.4	-	1.00	1.64	3.81	-	1.56	0.23	0.24	0.05	
São Jose dos Campos/São Paulo	Feb. 2004-Feb. 2005	15.7	-	0.36	0.37	2.17	0.96	0.34	0.46	0.30	0.03	[100]
Araraquara/São Paulo	April 1999-Feb. 2001	-	-	0.18	0.38	1.58	0.26	0.07	0.38	0.16	0.03	[101]
São Paulo/São Paulo	13 May-19 July, 2002	11.9	-	0.11	0.43	1.20	0.30	0.13	0.14	0.10	0.02	[102]
São Paulo/São Paulo	June 2007-August 2008	28.1	10	0.24	1.22	3.09	1.25	0.24	0.25	0.08	-	[85, 86]
Rio de Janeiro/Rio de Janeiro		17.2	3.4	0.11	0.56	1.91	0.80	0.21	0.18	0.04	-	
Belo Horizonte/ Minas Gerais		14.7	4.5	0.04	0.19	1.15	0.34	0.08	0.19	0.10	-	
Porto Alegre/Rio Grande do Sul		13.4	3.9	0.15	0.43	1.17	0.35	0.19	0.27	0.04	-	
Curitiba/Paraná		14.4	4.4	0.07	0.16	1.08	0.37	0.10	0.28	0.04	-	
Recife/ Pernambuco		7.3	1.9	0.15	0.11	0.61	0.18	0.33	0.14	0.05	-	

Table 5. Particulate matter ($PM_{2.5}$ or fine fraction) mass, black carbon (BC) and ions average concentrations in some Brazilian regions.

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		Trace elements Concentrations / ng m^{-3}								References
City/State	Sampling location	Mn	Fe	Zn	Cu	Cr	Al	V	Pb	
Rio de Janeiro/Rio de Janeiro	Urban area	5	307	20	35	<LOD	<LOD	2	<LOD	[103]
Campinas/São Paulo	Urban area	14.8	585	80.0	18.1	4.2	50.3	3.4	3.6	[104]
São Paulo/São Paulo	Urban + heavy traffic	6	181	75	10	2	55	2	16	[85, 86]
Rio de Janeiro/Rio de Janeiro		4	75	25	8	2	50	4	12	
Belo Horizonte/Minas Gerais		39	133	15	1	0.6	53	2	6	
Porto Alegre/RS		3	74	17	3	1	43	9	4	
Curitiba/Paraná		2	70	19	3	0.7	46	0.7	8	
Recife/Pernambuco		2	65	17	1	0.5	40	0.7	4	

Table 6. Trace elements concentrations in $PM_{2.5}$ (fine fractions) in some Brazilian cities.

City/State		Sampling location	PAH concentrations (ng m^{-3})	References
Canoas/Rio Grande do Sul		Roadside/traffic	1.32 (summer)	[105]
			2.02 (winter)	
Sapucaia /Rio Grande do Sul		Urban road/traffic	1.57 (summer)	
			3.05 (winter)	
Porto Alegre / Rio Grande do Sul		Metropolitan area	1.08 (summer)	[106]
			1.81 (winter)	
Salvador / Bahia	Lapa	Station bus	4.35 (winter)	[69]
	Aratu	Industrial center	2.94 (spring)	
	Bananeira	Non-vehicle influence	2.50 (spring)	
Cubatão / São Paulo		Industrial center	16.7 (spring)	[107]
São Paulo / São Paulo		Urban + heavy traffic	10.8 (winter)	[108]
Sapucaia do Sul, São Leopoldo and Novo Hamburgo / Rio Grande do Sul		Basin of the Sinos Region	1.52 (summer)	[109]
			1.68 (winter)	

Table 7. Atmospheric concentrations of total PAHs in some Brazilian cities.

5. Role of the biofuel use on secondary pollutants formation

Although the levels of primary air pollutants have decreased over the past 30 years in the MASP, secondary pollutants, like ozone and fine particles, frequently exceed established international and local air quality standards. Ozone and fine particles are secondary pollutants, products of VOCs, NO(x), and sunlight in the case of ozone and also sulfur oxides, ammonia, nitrogen oxides in the case of fine particles. Thus, it is very difficult to elaborate efficient strategies for their reduction. Since the frequent episodes of high concentrations of ozone

occurring in the MASP are primarily associated with vehicular emissions, some reports in literature examined the impact that the implemented control program for mobile emissions (PROCONVE) had on tropospheric ozone concentrations and evaluate the impact of using reformulated gasoline-ethanol blend (gasohol) and of hydrous ethanol on the ozone formation [88-93]. Studies related to the formation of fine particles are more sparse, Albuquerque et al. [94] analyzed the impact of reducing the sulfur content in the diesel and the secondary formation of sulfate-nitrate-amonnium system, showing that an increase in the nitrate-ammonium formation may occur while the decrease in the sulfate-ammonium system occurs.

Sanchez-Ccoyllo et al. [92] evaluated the impact of the PROCONVE implementation based on an episode of high surface ozone concentrations that occurred in the MASP during March, 2000, employing the California Institute of Technology/Carnegie Mellon University three-dimensional photochemical model (CIT model [95-97]). In this work, different scenarios of emissions were considered according to the implementation of the PROCONVE. Scenario 1 assumed that all vehicles in the fleet were operating within PROCONVE guidelines. Scenarios 2 and 3 considered hypothetical situations in which PROCONVE had not been implemented. Scenario 2 established the premise that all vehicles were using pre-1989 technology, whereas scenario 3 allowed the existence of technological advances. That work showed that tropospheric ozone concentrations predicted for scenario 2 (vehicles pre-1989 technology) were higher than those predicted for scenarios 1, 3, and for the base case. The authors demonstrated that the PROCONVE had great influence on the improvement of air quality concerning ozone in MASP. In another studied developed by Sanchez-Ccoyllo et al. [93], the analysis was concentrated in the meteorological impacts on the ozone formation. Three meteorological variables: mixing height, wind speed, and air temperature, were considered in the study. The study also evaluated the role of having a reactive hydrocarbon (RHC) limitation or NOx limitation configuration on ozone formation in the MASP. In addition, NOx and RHC emission inventory reductions were used to evaluate their sensitivities with the CIT model. The results showed that changes in mixing height, wind speed, and air temperature input files have the greatest effect on peak ozone production, and the isolated effect of RHC emission reduction lead to 26% lower ozone levels compared to the base case. Based on the results of this study, the authors concluded that reductions on RHC emission could provide the best scenario for promoting lower ozone concentrations in the MASP. In agreement to these results, Orlando et al. [91] showed that the occurrence of high ozone production is more dependent on VOC in a study employing the trajectory model OZIPR together with the SAPRC chemical mechanism. In that work, five base-cases were created to verify the variation in maximum ozone concentration related to the ozone formation potential of each VOC that was injected in the airbase. The NO(x) and VOC emissions were independently and simultaneously reduced by 5%, 10%, 20%, and 30% to induce variations in ozone formation and the results showed that the most frequent compounds found among the ten main ozone precursors in Sao Paulo, using the reactivity scales created from the five base-cases, were formaldehyde, acetaldehyde, propene, isoprene, cis-2-butene, and trans-2-butene, with formaldehyde being always the main ozone precursor. In addition, the simulations data showed that an efficient strategy to decrease ozone concentrations in the MASP would be to reduce the total VOC emissions, while the same

strategy is not possible for NOx, since the reduction of these pollutants would increase ozone concentrations.

The impact of the use of reformulated gasoline/ethanol blend (gasohol) or hydrous ethanol on the ozone formation was evaluated in a study conducted by Martins and Andrade [89]. In this work, a three-dimensional photochemical model was employed to estimate the sensitivity of ozone formation and evaluate the implementation of emission scenarios, considering various fuel formulations in the MASP. Six scenarios were analyzed in the work; scenarios 1 to 5 involved different reduction scenarios in the compounds found in gasohol at different proportions related to the base case emission inventory, and the scenario 6 specified that the entire LDV running in the MASP would burn hydrous ethanol. The results showed that in scenario 3 (reductions in olefins, aromatics, and benzene) and scenario 5 (reductions in the five species that are associated with higher ozone sensitivity), ozone concentrations were below the national standard only at the air quality monitoring stations (not domain-wide). In addition, these results suggest that implementing scenario 6 (entire LDV fleet burn hydrous ethanol) would improve air quality in the MASP. In contrast, the work developed by Salvo and Geiger [98] suggest that the use of ethanol in flex-fuel vehicles has a negative effect on air quality as regards the formation of ozone. Their work reports the consequences of a shift in fuel use in the MASP, brought on by large-scale fluctuations in the price of ethanol relative to gasohol between 2009 and 2011. The work uses highly spatially and temporally resolved observations of road traffic levels, meteorology and pollutant concentrations, together with a consumer demand model, to show that ambient ozone concentrations felt by about 20% as the share of flex-fuel vehicles burning gasohol rose from 14% to 76%. On the other hand, in this work data suggest that NO and CO concentration increased. Thus, considering that tropospheric ozone production over MASP is hydrocarbon-limited, high NOx emissions (from gasohol burning) resulted in reductions in ambient ozone. These results are consistent with modeling studies previously, which concluded that the atmosphere in the MASP is VOC-limited [89, 91-93].

6. Concluding remarks

Almost 30 years after the creation of Brazilian Motor Vehicle Air Pollution Control Program (PROCONVE), results show that the adoption of increasingly restrictive phases was successful and environmental concentration data show a clear downward tendency for several pollutants over past years, except for ozone and fine particles. The reduction on concentrations of these atmospheric pollutants became the big challenge for the public policies to elaborate efficient control strategies in urban areas of Brazil.

The Brazilian experience demonstrates how the impact of vehicular emissions can be reduced with the use of biofuels associated with technological developments. Results addressed in studies conducted in Brazil demonstrate that, although a considerable increase occurred in the number of LDV able to run on hydrous ethanol, and the increased use of biodiesel by HDV, key technological improvements in the design of the vehicles mitigated increases in the emissions of pollutants such as aldehydes, CO, and NOx.

7. Abbreviations

BC, black carbon; CETESB, São Paulo State Environmental Protection Agency; GHG, greenhouse gas; HC, hydrocarbons; HDV, heavy-duty vehicles, LDV, light-duty vehicles; MASP, metropolitan area of São Paulo; NOx, nitrogen oxides; PM, particulate matter; PROCONVE, Brazilian Motor Vehicle Air Pollution Control Program; VOC, volatile organic compounds.

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Author details

Thiago Nogueira[1*], Denise de Sales Cordeiro[2], Rodrigo Alejandro Abarza Muñoz[2], Adalgiza Fornaro[1], Antonio H. Miguel[3] and Maria de Fatima Andrade[1]

*Address all correspondence to: thiago.nogueira@iag.usp.br.

1 Department of Atmospheric Sciences, Institute of Astronomy, Geophysics, and Atmospheric Sciences, University of São Paulo (IAG/USP), Brazil

2 Institute of Chemistry, Federal University of Uberlandia, Brazil

3 A. H. Miguel & Associates, Pasadena, CA, USA

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