Influence of Brazilian Gasoline Sulfur Content on Regulated Pollutant Emissions

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ABSTRACT

This paper presents an experimental evaluation of the sulfur content influence, at 50 mg/kg (S50) and 10 mg/kg (S10) levels of Brazilian commercial gasoline with 27% in volume of anhydrous ethanol (E27), on legislated emissions, aiming for the 2025, L8 phase of Proconve (Air Pollution Control Program by Motor Vehicles). A comprehensive test program was carried out to investigate sulfur effects on the emissions of current and new vehicles.

Urban cycle instantaneous emissions of seven flex-fuel vehicles from Proconve phases L4 to L7 were assessed. Sequential tests were also carried out for mileage accumulation in L6 and L7 vehicles, to investigate a possible catalyst saturation with progressive increase in emissions. Lastly, emissions durability tests were performed using a burner for accelerated aging of the catalyst system from an US EPA Tier 3 - Bin 70 vehicle, which is approximately equivalent to the future Proconve L8 - Bin 50. Results showed similar behaviors between S50 and S10 gasolines in terms of regulated pollutant emissions for all evaluated vehicles and test conditions.

INTRODUCTION

In 2018, Brazilian National Environment Council – CONAMA published Resolution 492/2018 [1] establishing new Proconve phases L7 and L8 for light-duty vehicles entering into force, respectively in 2022 and 2025.

Subsequently, the Brazilian National Agency of Petroleum, Natural Gas and Biofuels – ANP created a working group to debate about the effect of gasoline sulfur content on pollutant emissions of new vehicle technologies implemented to achieve new Proconve limits.

Currently, some markets abroad like the USA adopt sulfur content of 10 mg/kg as an average for gasoline production but allows maximum limit of 80 mg/kg. It is important to warn that the emission limits foreseen for phase L8 are less stringent than those applied in USA EPA Tier 3. Moreover, Brazil has lower emission durability requirements, 160,000 km, when compared to the USA, 160,000 miles (240,000 km).

This paper presents the results of an experimental set of tests using commercial gasoline with different sulfur levels and flex-fuel vehicles. Tests were carried out with commercial gasoline sulfur content of 50, 30 and 10 mg/kg, to investigate the effects on the instantaneous vehicle emissions and on the catalyst sulfur accumulation using vehicles from different Proconve phases. Additionally, the catalysts durability was assessed by accelerated aging procedure in a burner, using an USA EPA Tier 3 – Bin 70 flex-fuel vehicle, approximately corresponding to the future Proconve L8 – Bin 50 in Brazil.

METHODOLOGY

As previously stated, three different methodologies were applied in this study to assess the sulfur content effect on vehicle emissions. The focus was to observe how fuels with 50 and 10 mg/kg, hereafter identified as “S50” and “S10” gasolines, would affect the instantaneous pollutant emissions during a driving cycle run, how it could impact the sulfur accumulation into catalysts, with possible emissions raises, and to observe effects on vehicle emission after catalyst system aging equivalent to 160 thousand km.

INSTANTANEOUS EMISSIONS - The evaluation of regular E27 gasoline sulfur content on instantaneous emissions was carried out in representative flex-fuel vehicles of Proconve phases L4, L5, L6 and L7. Additionally, a S30 gasoline was included in the instantaneous emission comparisons with S50 and S10.

Table I highlights some information of the seven flex-fuel vehicles used in this stage. They represent six different manufacturers (F1-F6), encompassing varied mileage and engine types, with PFI (Port Fuel Injection) and GDI (Gasoline Direct Injection) technologies, and different volumetric capacities. Note that for manufacturer 1 (F1), two models were tested (M1 and M2).

Table I. Vehicles used in the instantaneous emissions tests.

ID	*Proconve Phase*	*Model Year*	*Engine Type*	*Mileage (km)*
F1-M1	L4	2007	2.0 PFI	80,000
F2	L5	2013	1.6 PFI	21,000
F3	L6	2016	1.6 GDI Turbo	13,000
F1-M2	L6	2020	1.6 PFI	10,000
F4	L7	2022	1.5 PFI	11,000
F5	L7	2022	1.0 PFI	6,000
F6	L7	2022	1.0 GDI Turbo	6,000

To avoid other fuel properties effects, test fuels S50, S30 and S10 were prepared with the same composition and ethanol blend (E27), differing only in sulfur content. They were obtained from a same base gasoline and doped with ethanethiol (C_2H_6S), that is a sulfur compound normally found in the Brazilian gasoline. All gasolines met the requirements established in the ANP specification defined in Resolution 807/2020 [2].

Urban emissions tests were conducted following the Brazilian standard NBR 6601 [3] protocol, that applies the EPA FTP-75 driving cycle. For L4, L5 and L6 vehicles, NMHC (non-methane hydrocarbons), NOx (oxides of nitrogen) and CO (carbon monoxide) were measured, while for L7 vehicles, the sum NMOG+NOx and CO were evaluated as required by Proconve. The NMOG (non-methane organic compounds) was calculated from the measurements of NMHC, aldehydes and unburned ethanol, according to Ibama (Brazilian Institute of the Environment and Renewable Natural Resources) Normative Instruction 22/2020 [4].

After each fuel change, the catalyst was regenerated according to CRC Report No. E-94-1 [5] (CRC – Coordinating Research Council - USA) procedure, to reduce sulfur content and start testing each fuel in the same condition. At least three tests were performed with each gasoline to provide a statistical comparison between the result means, using Analysis of Variance (ANOVA) technique with a 95% confidence level.

SULFUR ACCUMULATION - This procedure aimed to investigate whether the gasoline higher sulfur content can contribute to the catalyst saturation, leading to eventual higher S50 emissions levels when compared to S10. This research was carried out with vehicles F1-M2 (L6 PFI) and F4 (L7 PFI) presented in Table I, using the same E27 S50 and S10 gasolines as the instantaneous emissions step.

The procedure consists of sequential emission tests, without cold start, following the EPA FTP-75 urban driving cycle, using phase 1 for vehicle conditioning and performing the measurements in phases 2 and 3. At the beginning of the test sequence with each fuel, the catalyst was regenerated according to the CRC Report No. E-94-1 procedure. As there is no standard procedure for this type of evaluation, this method was based on a similar procedure presented by the automotive industry in the ANP Working Group.

NMOG+NOx and CO emissions were compared. NMOG was calculated from the NMHC measurement according to EPA CFR 40 – §1066.635 [6], that is the basis of IBAMA 22/2020 normative instruction, that includes an alternative NMOG determination method. Equations (1) and (2) were adopted to calculate the NMOG for FTP-75 cycle phases 2 and 3 respectively, being e_{NMOG}, the NMOG emissions, e_{NMHC} the NMHC emissions and VP_{EtOH} the anhydrous ethanol volume from gasoline.

$$e_{\text{NMOG-FTPcs-hs}} = e_{\text{NMHC-FTPcs-hs}} \cdot (1.1135 + 0.001 \cdot VP_{\text{EtOH}}) \quad (1)$$

$$e_{\text{NMOG-FTPht}} = e_{\text{NMHC-FTPht}} \cdot (1.0195 + 0.0031 \cdot VP_{\text{EtOH}}) \quad (2)$$

CATALYST AGING - The sulfur content effect on each catalyst deterioration was evaluated by aging these components in a burner test bench following the Standard Bench Cycle (SBC) as defined by the Brazilian standard NBR 16897 [7]. Two sets of catalysts and oxygen sensors were aged to a mileage equivalent to 160,000 km, one using equivalent E27 S50 and the other equivalent E27 S10 gasolines. This was necessary to expose the catalysts in the aging test bench to the same sulfur amount as during the vehicle full useful life. Both gasolines were also generated from the same fuel base, differing only by the sulfur content with the addition of thiophene (C_4H_4S), that is also a sulfur compound normally found in the Brazilian gasoline.

An USA flex-fuel vehicle was used for these tests. The vehicle corresponds to the EPA Tier 3 emissions phase, Bin 70 (mg/mi), equivalent to the future Proconve L8 phase, Bin 50 (mg/km), expected to enter into force in Brazil in 2025. The vehicle can properly run with E27 gasoline.

The vehicle was degreened for 6,000 km on chassis dynamometer, with its original catalytic converter system, using a commercial gasoline. Both test catalytic systems were degreened on burner, up to the equivalent of 6,000 km, using E27 S10 gasoline. After degreening, each catalytic system was mounted on the vehicle and two emissions tests were carried out.

Then, each catalytic system was aged, respectively, with E27 S10 and S50 gasolines, during 289.4 hours on the burner test bench, the calculated aging time to be equivalent to 160,000 km, following the NBR 16897 procedure. After the accelerated aging in burner, both systems were mounted back on the vehicle and two emissions tests were carried out as the final tests.

All emissions tests were carried out in the urban driving cycle from NBR 6601 (EPA FTP-75), using E22 S10 Brazilian standard gasoline for homologation. The acceptance criterion adopted for the emission tests is described in CRC Report No E-94-2 [8], which considers variations of up to 30% for HC emissions and up to 50% for CO and NOx emissions, in relation to the results mean.

RESULTS

This section presents the emission test results, referred to the instantaneous evaluations, sulfur accumulation and catalyst aging as described in the previous section.

INSTANTANEOUS EMISSIONS – The instantaneous emissions results with S50, S30 and S10 gasolines, from the seven vehicles listed in Table 1, are presented in figures 1 to 8. Mean values of at least three tests are registered and compared to the Proconve emission limits for each pollutant and phase (dashed lines). Error bars correspond to the 95% confidence intervals for each mean value.

Figures 1 to 3 present, respectively, the results of NMHC, CO and NOx emissions from the vehicles F1-M1 (L4 PFI) and F2 (L5 PFI).

From figure 1, it can be noticed that for both vehicles, the NMHC emissions with all test fuels are quite similar. The ANOVA analyses revealed that there are no statistically significant differences between the means of the S50, S30 and S10 gasolines.

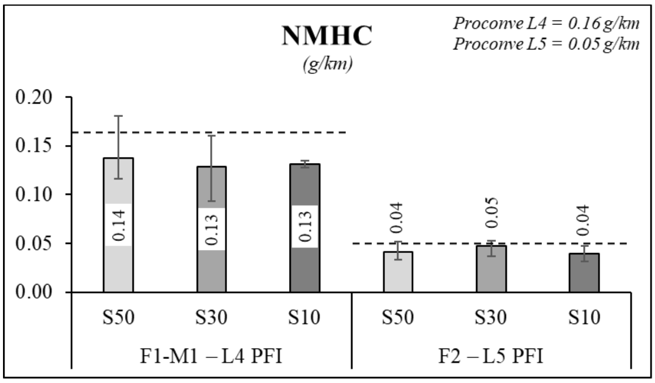

Figure 1. NMHC emissions from L4 and L5 vehicles.

The same behavior can be observed from figures 2 and 3 for CO and NOx emissions from L4 and L5 vehicles. Again, statistically significant differences were not detected from ANOVA analyses for all the comparisons between S50, S30 and S10 gasolines. The L4 vehicle CO emissions were above Proconve limit with all tested fuels, which can be related to its high mileage (80,000 km), considered close to the end of catalyst life for this phase.

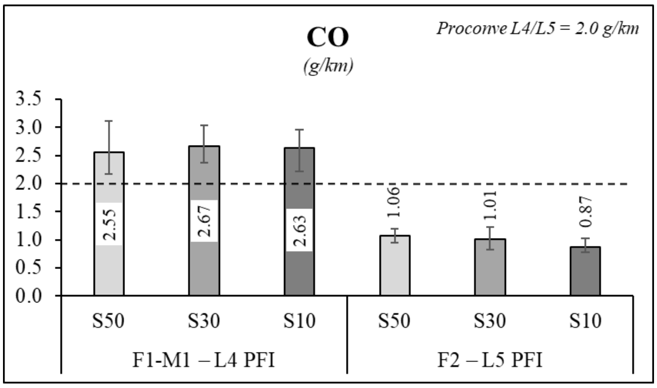

Figure 2. CO emissions from L4 and L5 vehicles.

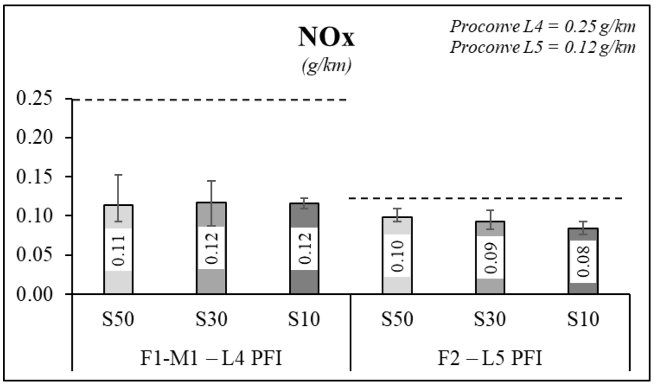

Figure 3. NOx emissions from L4 and L5 vehicles.

The set of emission test results from vehicles F3 (L6 GDI) and F1-M2 (L6 PFI) are presented in figures 4 to 6, for NMHC, CO and NOx respectively.

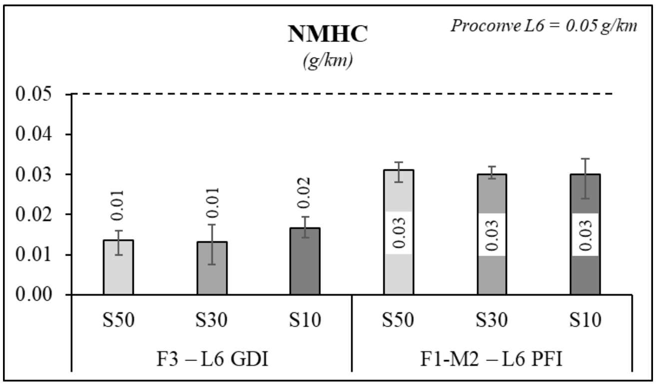

Figure 4. NMHC emissions from L6 vehicles.

Figure 4 shows that all NMHC emission results are very similar for all test fuels in both vehicles, without statistically significant differences observed by ANOVA analyses.

The analysis of CO emissions (figure 5) shows also very similar levels for all fuels in both vehicles but, in this case, the ANOVA technique pointed that the hypothesis of statistically significant differences between the results from the vehicle F1-M2 (L6 PFI) cannot be rejected. The emissions from S10 gasoline were 31% higher than those from S50 fuel. Regarding the F3 (L6 GDI) vehicle, no statistically significant differences were pointed out by the ANOVA analysis. All results were about one order of magnitude lower than the Proconve limits.

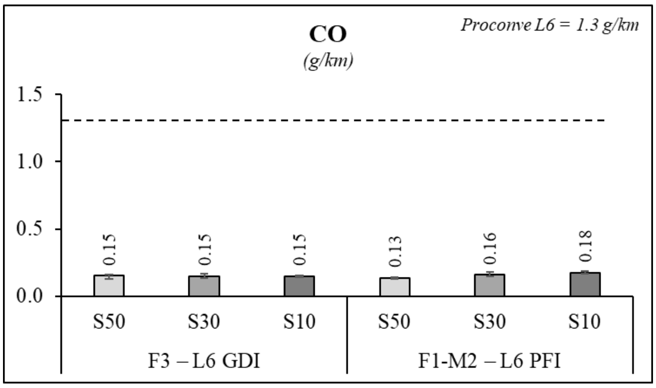

Figure 5. CO emissions from L6 vehicles.

For NOx emissions presented in figure 6, it can be noticed that, again, all results are quite similar for all fuels in both vehicles. Also in this case, no statistically significant differences were observed by ANOVA analyses.

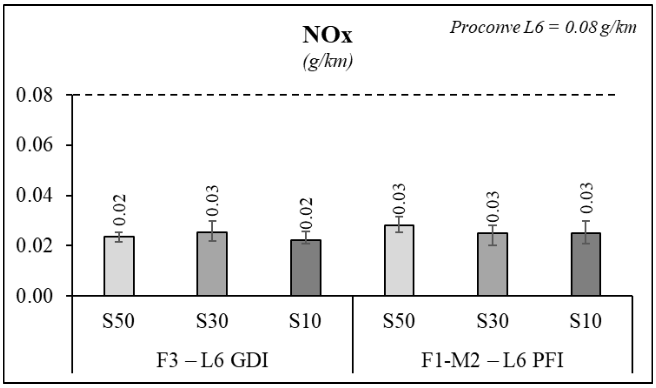

Figure 6. NOx emissions from L6 vehicles.

Figures 7 and 8 present the NMOG+NOx and CO emission results from the representative vehicles of the L7 Proconve phase, identified as F4 (L7 PFI), F5 (L7 PFI) and F6 (L7 GDI). These results regard to the new vehicle generation currently sold in Brazilian market from 2022.

Figure 7 shows that from the three L7 test vehicles, all NMOG+NOx emission results are similar with S50, S30 and S10 gasolines. The ANOVA analyses indicate that there are no statistically significant differences between the means of each vehicle.

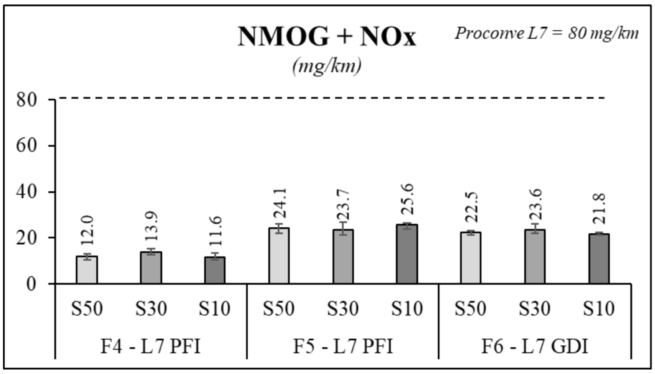

Figure 7. NMOG + NOx emissions from L7 vehicles.

Regarding CO emissions, presented in figure 8, the ANOVA analysis does not discard the hypothesis of statistically significant differences between the results from the vehicle F5 (L7 PFI). The S10 average result was 17% lower than the S50 one. For the other test vehicles, F4 (L7 PFI) and F6 (L7 GDI), no statistically significant differences were found by ANOVA analyses. All results were about one order of magnitude lower than the Proconve limit.

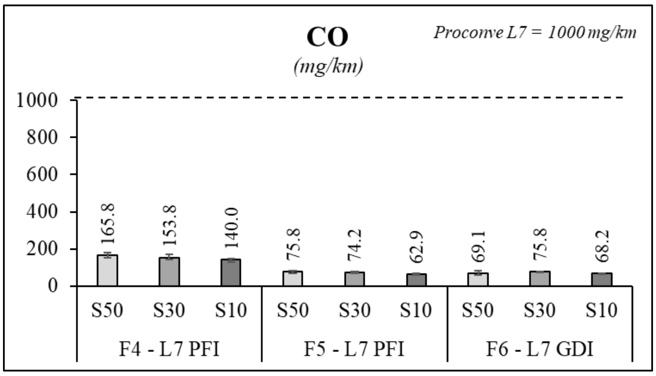

Figure 8. CO emissions from L7 vehicles.

SULFUR ACCUMULATION – As stated before, sulfur accumulation analyses were performed in two vehicles, i.e., F1-M2 (L6 PFI) and F4 (L7 PFI), by the comparison of S50 and S10 gasolines during a sequence of 8 FTP-75 driving cycle repetitions, which resulted in 144 km mileage accumulation for each test.

In figures 9 to 12, the results of NMOG+NOx and CO for both vehicles are presented. In these graphs, dark lines with filled circles represent S10 results while clear lines with empty circles represent S50 results.

The objective of this evaluation was to observe some eventual raise on emissions with the mileage accumulation and to compare the emission levels and behaviors between both fuel sulfur content. As can be noticed from figures 9 to 12, the result behaviors from both vehicles are quite similar with S50 and S10 gasolines for NMOG+NOx and CO emissions. Also, it is not observed any gradual increase of emission levels with the mileage accumulation up to 144 km.

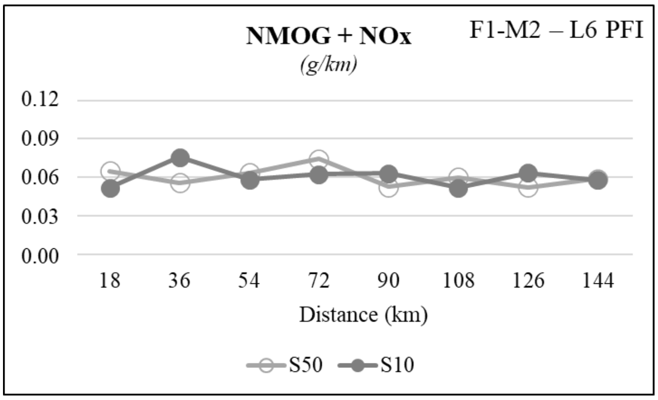

Figure 9. Effect of sulfur accumulation on NMOG+NOx emissions from L6 vehicle.

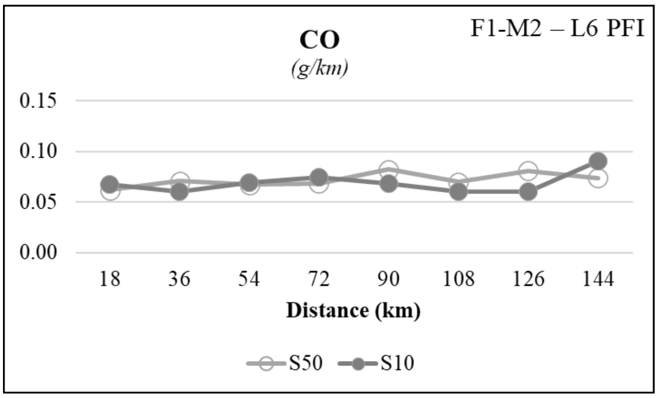

Figure 10. Effect of sulfur accumulation on CO emissions from L6 vehicle.

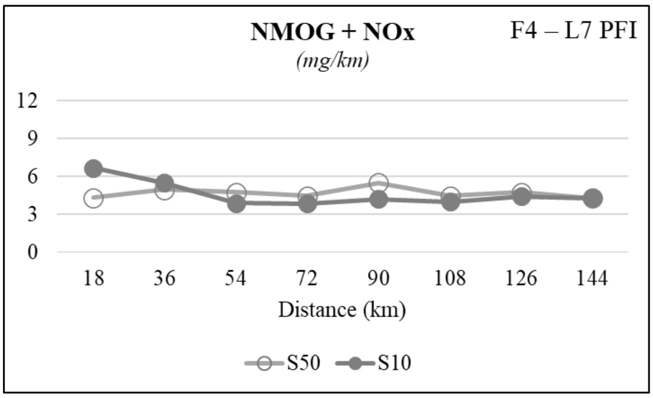

Figure 11. Effect of sulfur accumulation on NMOG+NOx emissions from L7 vehicle.

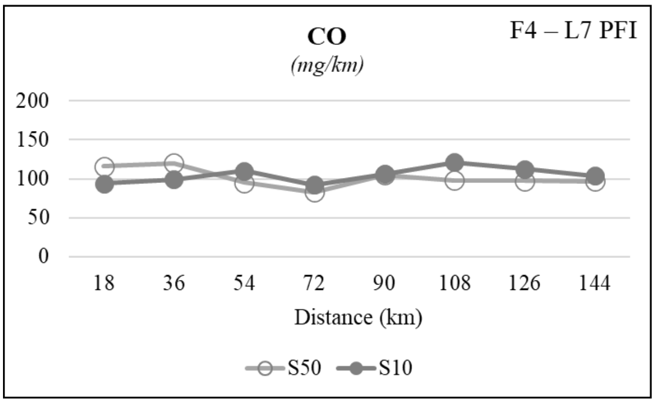

Figure 12. Effect of sulfur accumulation on CO emissions from L7 vehicle.

CATALYST AGING - Figures 13 and 14 show, respectively, the results of NMOG+NOx and CO emissions from the US EPA Tier 3 – Bin 70 (~ Proconve L8 - Bin 50) flex-fuel vehicle at 6,000 and 160,000 km, to evaluate the effect of sulfur on the deterioration of catalysts aged with S50 and S10 gasolines. Error bars correspond to the CRC acceptance criteria described before [8]. Dashed horizontal lines correspond to the emission limit foreseen for Proconve L8 - Bin 50 phase, from 2025.

As can be noticed, differences between the emission results with S50 and S10 gasolines at 6,000 km and 160,000 km are smaller than the adopted acceptance criteria for NMOG+NOx and CO. It can also be observed that both catalyst systems easily met the established L8 limits, even after the aging equivalent to 160,000 km.

Finally, it can be concluded that there were no differences in the deterioration of catalysts aged up to 160,000 km with S50 and S10 gasolines, regarding NMOG+NOx and CO emissions.

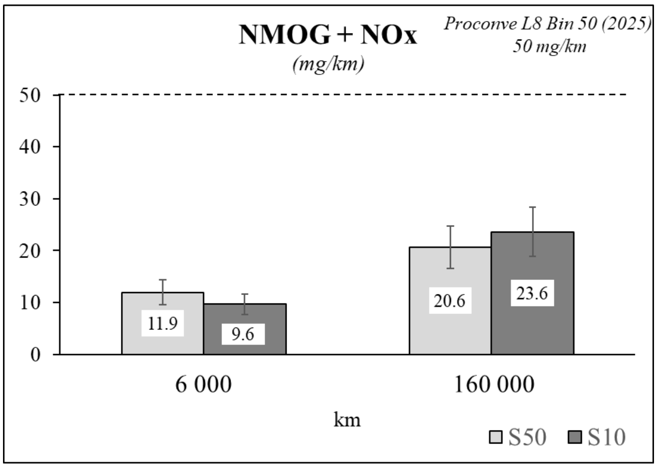

Figure 13. NMOG+NOx emissions from EPA Tier 3 Bin 70 (~ Proconve L8 Bin 50) vehicle at 6 000 and 160 000 km.

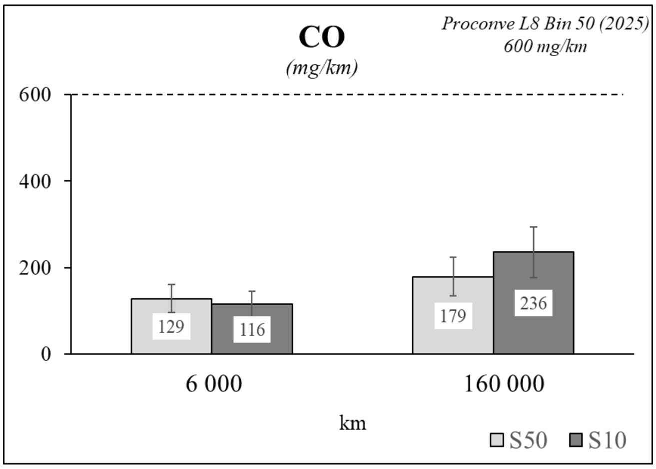

Figure 14. CO emissions from EPA Tier 3 Bin 70 (~ Proconve L8 Bin 50) vehicle at 6 000 and 160 000 km.

CONCLUSIONS

A comprehensive test program to evaluate the Brazilian commercial E27 gasoline sulfur content impact on vehicle emissions was successfully conducted, comparing sulfur levels of 50 mg/kg (S50) and 10 mg/kg (S10). Three different kinds of possible effects were assessed: instantaneous influence of catalysts sulfur poisoning during vehicle urban use; mid-term sulfur accumulation during vehicle sequential urban use; and sulfur influence on the aging of catalytic system, equivalent to full useful life.

Different vehicle technologies and ages were assessed to represent the current used vehicles fleet of Proconve L4 to L6 phases, the new vehicle technologies of L7 phase, while future L8 phase was represented by an EPA Tier 3 vehicle, tested in a USA laboratory.

Most of results showed that sulfur content changes from S50 to S10, including S30 intermediate level, did not significantly affect pollutant emissions behavior for all vehicle technologies and types of usage assessed.

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