

Air Pollution in the Brazilian Road **Transport and Its Environmental and Social** Consequences

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Abstract

The use of fossil fuels has been greatly increased since the eighteenth century with advent of the industrial revolution. Currently, the use of these fuels is responsible for, on average, 80% of energy generation in human society, producing large emission of pollutant gases and particulate material. Thus the transport sector is a major source of air pollution worldwide. This issue causes serious damages to the environment through phenomena such as acid rain, global warming and photochemical smog. Moreover, the emission of pollutants is also related to damages in human health. Brazil is a country with great territorial dimensions and its transport array is eminently by road, so it is a major consumer of fossil fuels, such as diesel, which has been producing serious environmental and social problems. Thus, this paper presents an analysis of the emission of gaseous pollutants and particulate matter from the transport sector (buses and trucks), gaseous pollutants such as NO_2 and SO_2 were detected in ppmv concentrations using electrochemical sensors. The composition constituents of the particulate materials emitted in diesel combustion and their respective concentrations were determined by X rays fluorescence spectrometry (XRF). The identified elements were: S, Fe, Si, Ca, Zn, P, Ni, Cr, Ti, Mn and Cu.

Keywords

Pollutant Gases, Particulate Materials, Electrochemical Sensors, X-Ray Fluorescence

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1. Introduction

The transport sector is an important segment of the global economy in which fossil fuels are used in large quantities. The use of this type of fuel contributes to worsening air pollution, which is one of today's main environmental problems, due to its correlation with severe atmospheric phenomena (global warming), causing the dreaded climate change [1]-[10], severely impacting biodiversity and modifying the planet biogeochemical cycles [11]-[19].

The transportation sector seriously impacts the environment due to its great expansion in recent decades and the use of diesel oil in a large scale. Diesel fuel, during its combustion, generates large amounts of greenhouse gases such as Volatile Organic Compounds (VOCs), carbon monoxide (CO), nitrogen dioxide (NO₂), sulfur dioxide (SO₂), carbon dioxide (CO₂), nitrogen monoxide (NO) and others [20]-[22].

The particulate material (PM) released into the atmosphere is generally invisible to the naked eye, but once treated collectively, these small particles form a mist which reduces the visibility. Burning fossil fuels is one of the most important sources of particulate material, especially in diesel engines [23]-[26] where its emission is related to the burning of diesel and lubricant oil, besides the bearing and engine materials wear.

According to Bosch [27], particulate material emission in diesel cycle engines is considerably larger than that in Otto cycle engines. Thus, once there is a large concentration of particulate material in diesel bus and truck exhausts, the chemical composition of these particles requires further investigation, since its composition is poorly known. Therefore, it is important to use sensitive and selective methodologies and techniques to identify pollutant gases and chemical species in the particulate material.

Brazilian transportation network is eminently by road, so this country presents enormous traffic congestion in large urban centers, which increases air pollution. There is also a government policy of encouraging the acquisition of vehicles for individual use rather than investing in public transport, which has caused chaos in major cities of the country. On June, 2013, a great number of protests started in São Paulo and quickly spread throughout many Brazilian cities, questioning the rising cost of tickets and the poor quality of the urban mass transportation [28]-[30]. Therefore, this option by road mass transport is reaching its limits, because it presents clear signs of saturation, which has been generating serious socio-political crisis in Brazil. The air pollution in large cities is another worrying factor due to the heavy use of road transport, which is seriously impacting population health [23]-[25] [31]-[38].

The operation of the Brazilian economy is closely linked to the maintenance of a large fleet of trucks and buses, since this country has a large territorial area and has prioritized the road transport. Brazilian domestic consumption of diesel is estimated to be around 40 billion liters per year, and 82.4% of this consumption is used only in the transportation sector [39].

The purpose of this study is to analyze the emission concentrations of NO₂ and SO₂ gases and determine the composition of particulate matter from exhaust of diesel vehicles (buses and trucks). These gases have an environmental importance to Brazil due to the fact that nitrogen oxides (NO_x) and VOCs in the presence of solar radiation, generate tropospheric ozone (O₃) [40]-[42], which is considered a secondary pollutant and a major constituent of photochemical smog. Brazil is a tropical country with intense solar radiation throughout the year, which eases the formation of O₃. NO₂ and SO₂ are generating acid rain [43] [44].

Several authors have pointed the harmful effects of air pollution on human health [33] [37] [45]-[47]. In Brazil, the situation is aggravated in the main metropolis, São Paulo, mainly by the transport model adopted in the country [24] [25] [31] [32] [34] [36]-[38] [42] [45]-[49].

In another initiative to reduce the use of diesel damage to the environment, Petrobras, a Brazilian state oil company, has developed a program to reduce the presence of SO_2 and sulfur in the formation of particulate material in large Brazilian cities. The D-500S diesel was then developed. This fuel, which is commercialized in Brazilian metropolitan regions, has 500 ppm of sulfur in its formulation, much better than the D-2000, which is commercialized in non-metropolitan regions (inside the country) and has 2000 ppm of sulfur in its formulation.

In this context, this paper presents a study of the emissions of pollutant gases and particulate material from diesel engines (buses and trucks) in the city of Campos dos Goytacazes, which is located in northern Rio de Janeiro State. In order to evaluate these emissions, electrochemical sensors were used. These devices detect gas molecules from the redox reaction between the sample and a reagent electrode inside the detector, generating electrical signals, which are proportional to the gas concentration [50].

The X-Ray Fluorescence Spectrometry technique was used to identify the chemical composition of particulate

material emitted in these engines. This technique premised to indentify the chemical elements and their concentration in samples from bus and truck exhaust. Once it is a non-destructive technique, it was possible to perform a simultaneous analysis of the many elements present in the samples, such as S, Fe, Si, Ca, Zn, P, Ni, Cr, Ti, Mn and Cu. It was also possible to detect the gases NO_2 and SO_2 in the ppmv range emitted by buses and trucks using an electrochemical analyzer.

2. Methodology

The gas samples collection was performed directly from the exhaust of diesel engines in two different engine operation modes. This methodology is adopted by organs of federal environmental supervision in Brazil as specific legislation [51]. The first one was in the non-accelerated operation mode, with engine rotation speed of about 3000 rpm. The second was in the accelerated operation mode, with engine rotation speed of about 6000 rpm. Each collection was performed during 2 minutes at regular intervals of 5 minutes in order to stabilize the motor.

The vehicles used in this study were randomly chosen in order to reproduce the real traffic conditions in a city. The trucks were evaluated in a federal highway (BR-101), which crosses the city and the buses were evaluated during their urban travel, within the boundaries of the city.

2.1. Electrochemical Sensors

The Electrochemical sensors used are present in the TEMPEST100® Analyzer (Telegan Gas Monitoring TP20729). The sensors detect the gas concentration from a redox reaction with a specific reagent electrode that is designed for each type of gas to be detected [50] [52] [53].

The analyzer has a suction pump that sucks the sample into its interior. Before contacting sensors, gases first pass through a hose containing a metal tip, which is placed directly on the output of the exhaust pipe of the vehicle. Then, gases go through a double filter system to contain material particles and condensed water vapor. Finally, the sample pass through a small opening, capillary type, and then it is spread by a selective hydrophobic barrier to reach the electrode surface [52] [53].

Within the sensor, there is a resistor connected to the electrodes. After the redox reaction, a current, proportional to the gas concentration, is generated. The reading of the results can be done in real time [50] [52] [53].

2.2. X-Ray Fluorescence Spectroscopy

The particles, which were retained in this filtering system in the TEMPEST100[®] Analyzer were collected, properly stored and taken for XRF analysis.

The X-ray fluorescence Spectroscopy (XRF technique) is considered to be the most useful and disseminated analytical method for determining the presence and the amount of elements present in a given substance. It uses the interaction between X-rays and the matter, and relies on the evaluation of intensity of the characteristic X-rays (number of X-rays detected per time unit) emitted by the elements of a properly excited sample. It is a non-destructive and rapid analysis, one of the most powerful and flexible techniques available for the analysis and characterization of materials, that have been developed during the last decades due to technological and digital advances [54]-[56].

The detection range of the elements vary according to instrument configuration, but typically covers the elements with atomic number equal or greater than 11 (sodium—Na). In some cases, with particular configuration, it is possible to detect lighter elements. It can detect concentrations from 100% to some ppm, reaching sub-ppm concentrations. Detection limits dependent on the element and the sample matrix, but as a general rule, with heavier elements, better detection limits can be achieved [54]-[56].

When an atom of an element present in the sample is excited, it tends to eject electrons from inner levels and, then, electrons from the outermost levels perform a quantum leap to fill the vacancy. Each electronic transition constitutes a loss of energy for the electron and the energy is emitted as a X-ray photon with characteristic energy and it can be used to identify the light emitting element. Basically X-ray fluorescence spectroscopy analysis consists of three steps: excitation of elements in the sample, scattering of emitted characteristic X-rays and detecting and measuring those X-rays.

The dispersion methods used in most X-ray spectrometers are classified into two types: wavelength dispersion

(WDXRF) and energy dispersion (EDXD). Each method has its own advantages and disadvantages. At the wavelength dispersion, the characteristic X-rays are selected by a crystal analyzer, according to their wavelengths, obeying the Bragg diffraction law. For the energy dispersion method, X-rays are selected through electronic pulses produced in a suitable detector, where the amplitudes of these pulses are directly proportional to the X-rays energies [54]-[56]. In this study, an energy dispersion spectrometer from Shimadzu was used.

3. Results and Discussion

According to the Traffic Department of the State of Rio de Janeiro (DETRAN/RJ), until March 2014, there were 14,299 registered diesel vehicles in Campos dos Goytacazes. In Brazil, this number is biggest than 320,000. This number has been increasing over the years in the city and in the entire country, as seen in the Figure 1 and Figure 2, respectively. Another worrying factor is the average age of these vehicles: most of them have over than 20 years of use. The scrapped fleet increases pollutants emissions due to the poor maintenance condition of these vehicles [51].

This experiment aimed to reproduce the dynamics of real traffic in a city. So, the choice of vehicles was random in order to check the present gases in situ, without the need to standardize the vehicles.

Table 1 shows the results for NO_2 and SO_2 emissions gases from the exhaust of 8 buses in the city of Campos dos Goytacazes. These buses are part of the city's public transportation fleet. They were manufactured between 1980 and 2006. The buses were supplied with D-2000, which is marketed in non-metropolitan regions (inside the country) and has 2000 ppm of sulfur in its formulation.

Analyzing NO₂ emissions, we can notice that this gas was emitted mostly in the accelerated operation mode than in the non-accelerated mode (**Figure 3**), possibly due to higher fuel consumption in higher engine rotation speed. The NO₂ concentrations emitted by the analyzed buses varied in a range of 4 - 868 ppmv. Once the minibuses have less powerful engines, they burn less fuel. Then, they emitted lower NO₂ concentrations.

Analyzing SO₂ emissions, one can notice that, in the accelerated operation mode, this gas also presented higher concentrations than in non-accelerated operation mode (**Figure 4**). Only two buses (1 and 3) presented an opposite trend behavior. The lowest concentrations of SO₂ emissions were also from the minibuses, probably because they have less powerful engines. SO₂ concentrations emitted by the analyzed buses were in a range of 9 - 362 ppmv.

Table 2 presents the results of NO_2 and SO_2 emissions from the exhaust of 8 trucks that passed by the BR101 highway, which crosses through the city of Campos dos Goytacazes, coming from large urban centers. These trucks were manufactured between the years of 1975 and 2010. In this case, the D-500S diesel was used by all



Figure 1. Increase in number of vehicles in Campos dos Goytacazes city by year.



Figure 2. Increase in number of vehicles in Brazil by year.





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venicie	Brand Year		NO ₂ (ppmv)		SO ₂ (ppmv)	NO ₂ (ppmv)	SO ₂ (ppmv)
1	Bus	Mercedes	1980	624	307	761	300
2	Bus	Mercedes	1981	359	280	669	354
3	Bus	Mercedes	1985	619	299	636	259
4	Bus	Mercedes	1989	657	301	868	362
5	Bus	Mercedes	2001	187	93	364	155
6	Minibus	Iveco	2003	4	9	6	9
7	Bus	Mercedes	2006	239	249	244	253
8	Bus	Mercedes	2006	268	172	330	191



Figure 4. Sulfur dioxide exhaust emissions from buses.

Table 2. NO_2 and SO_2 er	missions gases from t	the exhaust in trucks.
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Wabiala Davad		Vera	Low Rotation		Low Rotation	High Rotation	High Rotation
venicie	Dranu	i ear	NO ₂ (ppmv)		SO ₂ (ppmv)	NO ₂ (ppmv)	SO ₂ (ppmv)
9	Truck	Mercedes	1975	11	52	11	55
10	Truck	Mercedes	1977	88	15	286	0
11	Truck	Mercedes	1991	57	5	85	5
12	Truck	Wolks	2002	48	25	106	55
13	Truck	Ford	2005	92	24	136	10
14	Truck	Mercedes	2006	28	6	46	3
15	Truck	Volvo	2009	92	104	2	4
16	Truck	Scania	2010	235	100	153	45

trucks, which is commercialized in Brazilian metropolitan regions and has 500 ppm of sulfur in its formulation.

Analyzing NO₂ emissions, we can notice that, in most of the sample, this gas tended to be emitted mostly in the accelerated operation mode than in the non-accelerated mode (Figure 5), possibly due to higher fuel consumption in higher engine rotation speed. However, the vehicles 15 and 16 presented different behavior. The analyzed trucks emitted NO₂ gas in concentrations between 2 and 286 ppmv.

Analyzing SO₂ emission, only trucks 9 and 12 presented higher emission concentrations in the accelerated operation mode. The others showed different behavior. The trucks emitted SO₂ gas in concentrations between 2 and 104 ppmv (Figure 6).

If we compare SO_2 emissions on **Table 1** and **Table 2**, SO_2 gas emission is greater from buses than from trucks. This factor is possibly connected to the use of fuel, once the buses are part of the public transportation fleet and were supplied with Petrobras standard diesel (D-2000S), while the trucks driving along the BR101 highway came from metropolitan areas and were supplied with metropolitan Petrobras standard diesel D-500S. This behavior was also noted for NO₂ gas, once buses emitted this gas in higher concentrations than trucks.

 NO_2 and SO_2 were detected in most vehicles with high concentrations (ppmv) as shown in Table 1 and Table 2, leading to a serious environmental and social problem, since these gases are precursors of tropospheric ozone. Tropospheric ozone is a major constituent of photochemical smog, generates acid rain, reduces the ozone layer and it is harmful to human health.





Figure 6. Sulfur dioxide exhaust emissions from trucks.

The emission of particulate material is related with the burning of diesel fuel and lubricant oil and with the wear on the engine bearings and materials. Particulate emissions in diesel cycle engines are considerably larger than in Otto cycle engines. Table 3 presents various constituents of the soot, which was accumulated on the filters used in the gas collection from the exhaust of buses and trucks engines.

Elements such as Zn, Ni and Cu probably derived from the degradation of structural metal parts of the engine and are harmful to be inhaled by humans. Elements such as Mn, Cr, Fe, probably derived from the internal corrosion of stainless steel components, mainly chromium, which is a heavy metal, highly toxic for humans. Elements such as Si may be derived from a possible contamination of the sample with the environmental dust. P residues may come from the contamination of detergent and lubricant additives, while K and Ca may be residues of the catalysts, such as KOH and CaOH, respectively.

In **Table 3**, we can notice a difference in the composition particulate sulfur emitted in buses and trucks. In truck exhausts, this component presented lower concentration than in the bus ones. This difference is probably due to the fact that the fuel used by buses has a greater concentration of sulfur (D-2000S) than the fuel used by trucks (D-500S), which reinforces the need for public policies for reducing pollution.

Element	Concentrations of particulate per sample (wt%)			
	Bus	Truck		
S	52.67	30.08		
Fe	16.51	22.24		
Si	11.83	7.63		
Ca	9.00	23.82		
Zn	2.95	12.10		
Р	1.85	2.11		
Ni	1.37	0.29		
Cr	0.69	0.56		
Ti	0.62	0.44		
Mn	0.31	0.49		
Cu	0.18	0.24		

Table 3. Element analysis of a sample particulate by EDS-XRF.

4. Conclusions

Electrochemical sensors proved to be sensitive and selective to detect and quantify the gases NO_2 and SO_2 . Using electrochemical sensors, it was possible to measure these gases on the exhaust of buses and trucks in ppmv concentrations. X-ray Fluorescence Spectroscopy intended to identify the constituent elements of the soot from the bus and truck exhaust.

In Brazil, there are more than 1 million buses and trucks. Many of them with over 15 years of use are in bad conditions. In June 2013, this fact triggered popular manifestations challenging the increase in bus fares, considered much expensive with low service quality. These protests began in the city of São Paulo and have spread throughout the country, where millions of people crowded the streets of major Brazilian cities to manifest for improvements in the transportation sector.

The government has given priority to individual transportation, leading to increased car sales and consequently traffic congestion in large cities. This reduces the logistics of people transit and negatively impact important sectors of the economy. In the trucking industry, the option for the majority use of road transport generates difficulties in exportation of agricultural products, delivery delays and economic losses.

The implementation of public policies that prioritize quality public transportation, including trains, subways, light rail transit (LRT) and special lanes for buses is required. Furthermore, the government must establish strict environmental legislation to limit the emission of gases and particles by the transportation sector, encouraging the use of more environmentally sustainable fuels.

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