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RESEARCH ARTICLE

Determination of size-segregated elements in diesel-biodiesel blend exhaust emissions

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Abstract
This study was based on the determination of metals in particulate matter emitted by a typical diesel engine used by busses and trucks in Brazil. Emissions were sampled using a cascade impactor, and the engine was operated using diesel with 5% (B5), 10% (B10), 15% (B15), and 20% (B20) of biodiesel. The particulate matter was stratified in different sizes, i.e., 18, 5.6, 3.2, 1.8, 1.0, 0.560, 0.320, 0.180, 0.100, and 0.056 μm. Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, V, and Zn with concentrations within 10 to 1000 ng m^{-3} were determined. The results indicate a trend in the prevalence of lead, nickel, and chromium in coarse particles and nanoparticles in all blends of fuels. By comparing the results of B5, B10, B15, and B20 fuels, we can confirm that the addition of biodiesel to diesel promotes a reduction of emissions, and by comparing the behavior of the concentration of all elements analyzed, emissions by B10 and B15 fuels are similar, while B5 and B20 suffer significant changes during the process of combustion. Multivariate statistical analysis was used, and it indicates possible sources in three clusters, one for Ni, other for Cr-Mn, and the last one for other metals.

Keywords Emissions · Metals · Diesel · Biodiesel · Particulate matter · Nanoparticles

Introduction

Different types of fuels are used in Brazil, including gasoline with 25% ethanol, hydrated ethanol, compressed natural gas (CNG), diesel, and biodiesel, the latter being used on a large scale by busses and trucks. They account for 6% of the fleet but consume about 45% of the fuel produced. Heavy vehicles have high power and emission factors and also travel longer distances than light vehicles. In Brazil, vehicles undergo emission tests, according to Brazilian regulation PROCONVE (Air Pollution Control Program for Automotive Vehicles), to determine the criteria pollutant emission, such as carbon monoxide (CO), nitrogen oxides (NOx), carbonyls (RCHO), non-methane hydrocarbons (NMHC), and particulate matter (PM). In particular PM, the actual limits of phase 7 of PROCONVE (Euro 5) are 0.02 g kW h^{-1}, but for the engine used in this work (phase 5 of PROCONVE or Euro 3), the limit is 0.10 g kW h^{-1}.

In the specific case of biodiesel, there are several ongoing researches, because biodiesel has shown itself to be an excellent alternative fuel, being renewable, environmentally friendly and minimizing the greenhouse effect, when compared with diesel (Suzuki 2002; Weiss et al. 2000).

However, diesel/biodiesel blends can still emit toxic and harmful substances during combustion, such as some metals, known as being responsible for many diseases. Nowadays, Brazilian vehicles use B7 mixture (7% of biodiesel in a volume basis) and will use B8 in 2017, B9 in 2018, and B10 in 2019, and there is no concern about possible effects from non-criteria emissions, posing risks to the environment and population health. As possible, non-criteria emissions such as metals, carbonyls, polycyclic aromatic hydrocarbons (PAHs), ultrafine particles, and nanoparticles speciated reactive volatile organic compounds (VOCs), among others.

In the literature, we can find evidence to justify the importance of PM emission determination from engines operating

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with diesel and biodiesel blends. There are epidemiological studies showing the impact of PM on human health, especially PM under 10 μm, called PM_{10} (Künzli et al. 2000; Katsouyanni et al. 2001; Pope et al. 2002; Peng et al. 2005; Rainho et al. 2013a, 2013b, 2014).

Metals are usually emitted as oxides and other minor compounds such as sulfates, nitrates, and peroxides. They can form a unique particle itself or can be adsorbed in carbonaceous particles and organic compounds, such as PAHs and its derivatives (Institute HE 2002).

PM from diesel emissions is characterized by different sizes, including coarse micro-metric particles, ultrafine particles, and nanoparticles. It is known that the smaller the particle size the greater its penetration capacity in the respiratory tract and smaller particles can reach vital parts of the human body such as the lungs, liver, and brain (Rainho et al. 2013a, 2013b). Although the relationship between PM, toxicity, and genotoxicity is uncertain, it is suggested that the fine airborne particles are retained in pulmonary alveoli, clinging to the pulmonary epithelial cells, and through redox mechanisms can cause acute respiratory infection, stress, and oxidative damage to DNA, membrane lipids, and proteins (Dick et al. 2003).

Recent studies showed that urban atmospheres containing high levels of PM_{10} and $PM_{2.5}$ are correlated to high emission factors by gasoline and diesel vehicles, as well as stationary combustion processes (Ventura et al. 2017; Mateus and Gioda 2017).

There is great concern about the possible damages that these particles have on the environment. Among the elements most commonly observed in urban aerosol are Na, K, Ca, Al, Fe, Pb, Ni, Cr, Ti, V, and Zn, and a number of less abundant elements, such as U and Ce, are also observed (Sanderson et al. 2014), as shown in Table 1. These particles have several origins, especially from traffic, due to the use of fuels, lubricant oils, tires, additives, and catalysts (Liati et al. 2012, 2013).

The origins of these metals are various, as stated by Ulrich et al. (2012). Among the metals determined here, Ulrich et al. (2012) indicated that Cr, Ni, Cu, and Pb could originate from the abrasion in piston rings, cylinder liners, valve cams, and bearings in an extent of 0.1 to 1.0 mg km^{-1}. The same authors reported that Zn could be emitted up 0.1% of the lubricant oil consumed and Pb and Mn from diesel combustion.

These metals were determined because they can damage human health, depending on the concentration, despite some of them not being totally anthropic; in other words, some metals can be from natural sources.

The acute exposure to cadmium can possibly cause gastrointestinal inflammation, vomiting, and diarrhea. The International Agency for Research on Cancer (IARC) considers Cd and its compounds carcinogenic, because the inhalation of 5 mg m^{-3} over a short period causes destruction of lung epithelial cells, edema, tracheal bronchitis, and pneumonitis and longer periods of exposure cause lung tumors, emphysema, and chronic obstructive pulmonary disease.

Table 1 Elements in ultrafine particles and the main sources (Sanderson et al. 2014)

Emission sources	Elements
Diesel	Al, Ca, Cu, Fe, Mg, Mn, V, Zn
Gasoline	Sr, Cu, Mn
Lubricant oil	Fe, Ca, P, Zn, Mg
Vehicular catalyst	Fe, Mn, Ce
Marine diesel	Al, Ca, Fe, Ni, V, Zn
Break	Fe, Cu, Sn, Zn
Tire	Cd, Co, Cr, Cu, Fe, Mn, Pb
Street dust	Zn, Al, K, Fe, Na, Mn
Metallurgy	Fe, K, Na, Pb, Zn
Power generation	Ce, Fe, La, Na, K, V,
Incinerators	Cd, Pb, Sb, Zn

Chromium is bioaccumulative and can cause permanent eye damage. It is mutagenic due to its direct access to cells and it has high oxidation power (Anderson 1986).

Manganese is essential to good body functions, like in the bones, kidney, and liver. However, in high concentrations, it can cause damage to the central nervous system, is mutagenic, and causes DNA damage. It affects fertility through the absorption of manganese salts by the placenta. There are also reports linking the incidence of Parkinson's disease to exposure to manganese (Wexler 2014; Emsley 2011).

Copper poisoning symptoms in humans include renal failure, liver failure and coma, abdominal pain, dizziness, tachycardia, and digestive hemorrhage. There are reports that associate exposure to high levels of Cu with its accumulation in tissues can result in the condition known as Wilson's disease (in the brain and liver). In this particular case, the latent concern is with nanometric particles, due to their low granulometry allowing them to reach the brain. This is much more important since it can directly affect the emergence of the disease (Zhang and Wexler 2004; Emsley 2011).

Molybdenum is essential to human health, but high exposures of this metal are associated with an increase in uric acid and the appearance of joint pain. Nickel, lead, and vanadium are carcinogenic (Zhang and Wexler 2004; Emsley 2011).

This work is a contribution to determine non-crustal metals in different particle sizes from the emission of a typical urban diesel engine using diesel/biodiesel blends. A micro-orifice uniform deposit impactor (MOUDI) was used to sample the vehicle exhaust, and metals were analyzed by inductive coupled plasma and atomic emission spectroscopy (ICP-AES).

Materials and methods

Experimental facilities

A typical engine of the urban bus fleet of Brazilian cities was used, as described in Table 2.

A 3-m long and 2″ diameter steel tube was attached to the end of the exhaust pipe, where the samples were taken without dilution of the exhaust gases at a sampling temperature between 52 and 54 °C, as required by Brazilian test procedure (ABNT 2000). Samples were collected at the beginning, at the middle, and at the end of the tube, and no loss was found. Changes were observed in the size of particles depending on the sampling position inside the tube. A sampling scheme is provided in Fig. 1.

Two sampling methodologies were used. The first one used a sampling time of 30 min with the engine at 700 rpm. This first approach was used to estimate the emission factors and adjust the sampling methodology, sample treatment, and chemical analysis. The final optimized methodology used 60 min with the engine operating at 700, 1000, and 1300 rpm, and the samples were collected in triplicate.

Fuels tested

The engine was previously heated for 30 min and operated with commercial diesel with 5% of biodiesel (B5), S50 standard (50 ppm of sulfur). Then, after using for the first tests, the remaining volume in the fuel tank was volumetrically measured and other blends were made with 10, 15, and 20% biodiesel: B10, B15, and B20, respectively. The biodiesel was produced from soybean using transesterification using potassium hydroxide and ethanol in our laboratory, and some physical-chemical properties were measured, as detailed in Table 3.

Sampling procedure

Sampling was carried out using a ten-stage MSP 120R nano MOUDI impactor (micro-orifice uniform deposit impactor), and in each stage, 0.2-μm fiberglass disks with 47 mm in diameter were used. The sampling flow was 30 L min^{-1} using a 35-cm ¼ PTFE tube inserted directly into the exhaust tube. The stages collected particles with 18, 5.6, 3.2, 1.8, and 1.0 μm and 560, 320, 180, 100, and 56 nm.

After sampling, the fiberglass disks were immediately treated following the IO 3.1 methodology (U.S.EPA 1999), with a HNO_3 3:1 HCl solution, ultrasound digestion for 3 h at 70 °C, centrifugation for 30 min, rest for 24 h, vacuum filtration, and rotary vapor concentration. The final volume was diluted to 30 mL with HNO_3 3% solution.

The recovery test was done with blank filters in triplicate tests, one for each MOUDI stage by adding five 20-μL aliquots of a 6-mg L^{-1} standard solution, containing all analytes. All filters were subjected to the same sample treatment. No recovery tests were done for real samples. According to U.S.EPA (1999), results are accepted from 75 to 125% recovery in addition to standard blank filters and from 80 to 120% recovery for real samples.

Table 2 Engine characteristics

Manufacture	Cummins
Cylinders	6
Model	Euro III
Year	2008
Power	140 kW
Displacement	4.8 L
Torque	680 nm at 1400 rpm

Chemical analyses

Chemical analyses were performed in the first campaign using a ICP-AES Horiba Jobin Yvon Ultima 2 and in the second campaign using a ICP-AES Perkin Elmer Optima 8300DV, and external calibration was used with certified standards (Ultra Scientific Inc.), all diluted in a HNO_3 3% *v*/*v* solution, and the calibration range used was 1 to 100 μg L^{-1}. The standards and samples were analyzed in triplicate. The conditions of the ICP-AES analysis were as follows: power rating (1200 W), normal speed pump hose (24 rotations min^{-1}), coating gas time (15 s), flow nebulizer (20 mL min^{-1}), nebulizer pressure (2.5 bar), and wash time (40 s). The wavelengths were chosen by interfering tests and all results have background correction and were done with Gaussian mode.

The wavelengths, voltage, integration time, and recovery results for each element are presented in Table 4, and also the limit of quantification (LOQ). Cerium and antimony showed recovery values lower than 75% and were not determined in the emission samples. Zinc and barium were also present in the blank fiberglass filters and the blank value was reduced from sample values, but the blank filters presented higher concentration of barium than the samples. This fact made the determination of barium impossible. Cobalt results were below the LOQ in all samplings.

Data treatment

In order to understand possible similar origins for some elements, multivariate statistical approaches were applied. This procedure allows the analysis of several variables simultaneously, and in this way, new information is visualized that could not be obtained by the univariate statistic, especially in the presence of many variables (Wehrens 2011). Another goal of multivariate statistics is to reduce the dimensionality of the

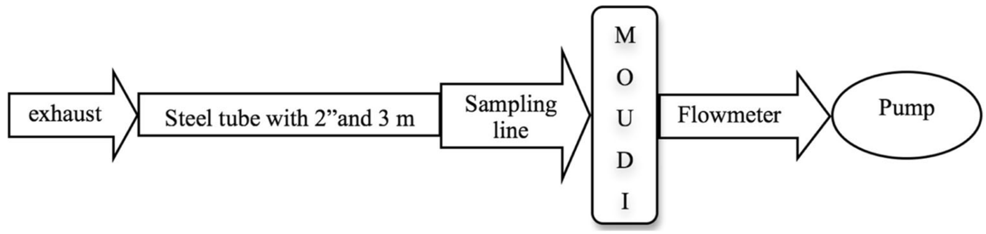

Fig. 1 Details of the sampling procedure

data, in the form of clusters that make it easier to see how the data are correlated.

Principal component analysis (PCA) consists of reducing the size of the set of original variables without loss of information. This technique groups the variables (components) according to their variances and behavior within the data population (Wehrens 2011). It is a method of analysis that projects the multivariate data into a smaller space than the original data set, without changing the relationships between the samples. This reduction in data dimensionality is represented by the main components (PC), which reproduce the original set using a combination of variables describing the data trend (Ferrer-Riquelme 2010).

The importance of a component is assessed by its contribution, i.e., by the proportion of total variance explained by the component. This is obtained by calculating the scores for each main component, which are organized through tables or graphs that allow the comparison between individuals. In general, a Gaussian distribution is used initially, and then the non-parametric Kruskal-Wallis test that allows to compare independent samples (Miller and Miller 2010) is applied. This test is considered an alternative of ANOVA (variance analysis), applicable for non-parametric data (data out of the normal distribution), and an extension of the Mann-Whitney *U* test applicable to only two sets. The test assumes that the distribution of results is random and that the populations being compared are independent. The test allows us to verify the null hypothesis by assuming that all data sets have the same distribution by calculating the level of significance of the deviation (p). The *p* value is accepted when greater than 0.05 for the null hypothesis that can not be rejected, and therefore, there is no reason to consider that the samples are statistically different. The value of *p* is related to the confidence of the conclusions obtained, and thus, a *p* value of 0.05 indicates that there is a 5% probability that the null hypothesis is valid. R language version 3.3.1 (Core Team 2016) was used for the processing of the study data.

Table 3 Biodiesel and diesel details

Properties	Methodology	Diesel	Biodiesel	Units
Acidity	ASTM D664	ND	0.18	mg KOH g^{-1}
Density	ASTM D1298	851	880	g cm^{-3}
Viscosity	ASTM D445	3.3	5.5	mm^2 s^{-1}
Moisture content	ASTM D6304	37	81	mg kg^{-1}
Corrosive to copper	ASTM D130	0.3	0.9	
Flash point	ASTM D93	45	106	°C
Plugging point	ASTM D6371	5.1	− 1.0	°C
Total free glycerol	ASTM D6584	ND	0.141	%
Ester content	EN 14103	ND	93.1	%
High heating value	ASTM D193	10,100	ND	kcal kg^{-1}

ND not determined

Results and discussion

The filters from each MOUDI stage were grouped in order to obtain enough mass of analytes to be analyzed, as follows: coarse particles (18, 5.6, and 3.2 μm), fine particles (1.8 and 1.0 μm), ultrafine particles (560 and 320 nm), and nanoparticles (180, 100, and 56 nm). The results are presented in Fig. 2 for coarse particles, in Fig. 3 for fine particles, in Fig. 4 for ultrafine particles, and in Fig. 5 for nanoparticles.

The triplicates of each test showed a maximum deviation value of 6.2% for Cd, and the average deviation value for all metals was 3.2 ± 2.5%.

As can be seen in Figs. 2, 3, 4, and 5, comparing the values of *y* scale, the results showed higher emissions for coarse particles and similar results for fine particles, ultrafine particles, and nanoparticles. The elements with higher concentrations were lead, mainly in B5 and B10 in coarse particles, and lead and nickel in all blends, in fine and ultrafine particles. However, chromium becomes a protagonist element, with high concentrations in ultrafine particles, starting in fuel B10. In nanoparticles, fuel B5 has high concentration of three elements: lead, manganese, and chromium. Mn and Cr show the same behavior also in all the other blends (B10, B15, B20).

Although the minimum emission limit for each metal that impacts the environment and health of the population is unknown, it is believed that emission levels in the microgram per cubic meter range can be severely damaging, assuming that nanometric particles have the capacity to reach the inner parts of human body. It is therefore of great importance to know in detail the minimum concentration that can be present in ambient air and in the emissions of vehicles using different fuel types.

Table 4 Results for the recovery tests and LOQ for each metal

Metal	Wavelength (nm)	Voltage (mV)	Integration time (s)	Recovery (%)	LOQ (ng m^{-3})
Cd	214.438	730	2.0	92.2	33.1 ± 1.8
Cr	267.716	990	2.0	94.0	37.0 ± 2.0
Cu	224.700	890	0.5	88.6	34.5 ± 1.8
Mn	257.610	680	0.5	89.1	39.3 ± 2.0
Mo	202.030	870	1.0	79.9	47.5 ± 2.5
Ni	231.604	860	2.0	97.4	37.7 ± 2.0
Pb	220.353	960	2.0	77.2	43.5 ± 2.2
V	292.402	920	0.5	82.0	47.1 ± 2.5
Zn	206.200	990	1.0	93.7	32.3 ± 1.8

Results from vehicles from Taiwan (Wang et al. 2003), using a dynamometer bench for all PM sizes, showed higher concentrations of metal emissions than our tests. Comparing data from different biodiesel blends, we can confirm that the addition of biodiesel promotes a reduction in metal emission, as higher metal emissions in the B5 are observed. Regarding B10, B15, and B20, the difference is not pronounced, decreasing the emission to a lesser extent.

Cadmium showed the lowest concentration among elements, and its presence is more pronounced in B5 fuel for coarse particles. For fine particles, Cd was found only in B5 and B10. For ultrafine particles and nanoparticles, Cd was found only in B5. Considering all blends and engine speed, coarse particles contain 72.9% of the emissions and fine particles 14.0% (SM 1).

Chromium and manganese are the elements of major concern, as they were found in higher levels compared to others, with higher emissions in B5 and a slight decrease for the other blends. It is noteworthy the highest emission for all fuels in nanoparticles (30.4% for Cr and 37.8% for Mn) and coarse (36.5% for Cr and 36.9% for Mn) particles. It was expected that the contents of Cr and Mn would be high because these metals are common in the PM from diesel/biodiesel engines (Weckwerth 2001). Moreover, they are also common in ultrafine particles, as reported by Sanderson et al. (2014). Adachi and Tainosho (2004) also reported that half of the nanometric particles contain these metals in their structure (SM 2 and 3).

Results for Cu indicated that 75.9% of the emissions are concentrated in coarse particles and similar content for the other PM sizes. Levels of Cu emissions are similar to Cr and Mn. Regarding biodiesel use, the emissions are well distributed on B5, B10, and B15, with a reduction with the use of B20 (SM 4).

Following a similar behavior, molybdenum presented elevated emissions only in B5 and 73.4% of the emissions are concentrated in coarse particles. These results also show that the use of biodiesel will result in significant reductions in Mo emissions, as no Mo was found in ultrafine particles and nanoparticles. Kukutschová et al. (2011) reported that the presence of Mo may occur in PM from diesel engines, but they did not report in which particle size. Weckwerth (2001) also describes that German vehicles have Mo in their emissions. This may explain the incidence of Mo in B5 fuel in ultrafine particles (SM 5).

Nickel showed higher emission in B5 and B10 fuels and an intermediate emission in the B15 and lower values for B20. Weckwerth (2001), Sanderson et al. (2014), and Springer

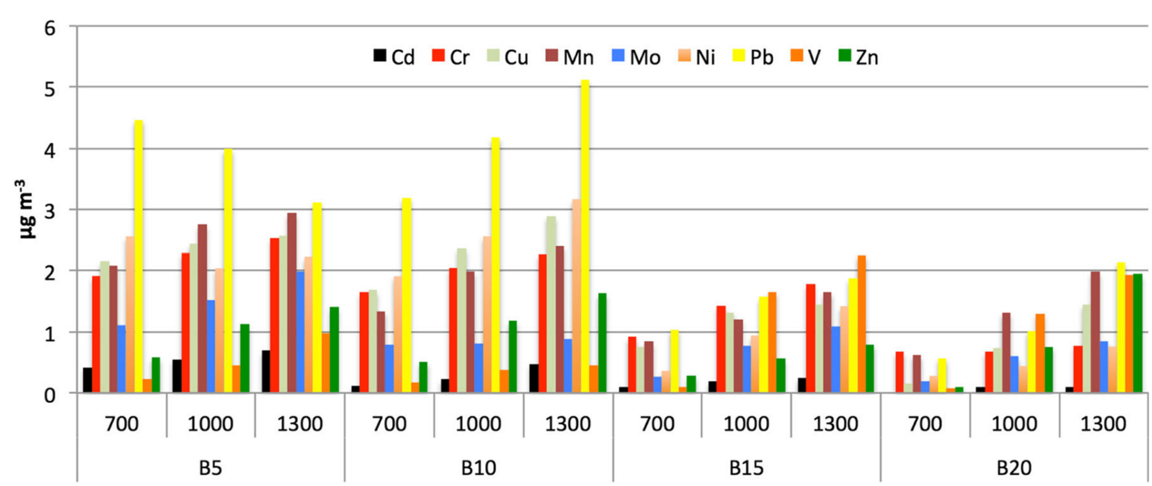

Fig. 2 Results for the emissions of coarse particles for B5, B10, B15, and B20 in different engine speeds (700, 1000, and 1300 rpm) for each metal

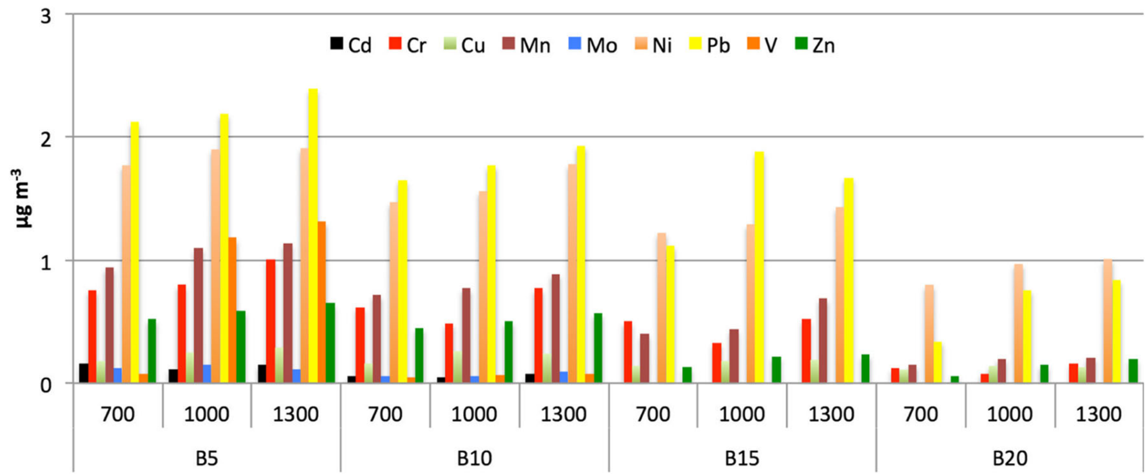

Fig. 3 Results for the emissions of fine particles for B5, B10, B15, and B20 in different engine speeds (700, 1000, and 1300 rpm) for each metal

(1997) reported that the presence of Ni is common in four-stroke diesel engines and fuel. Cernuschi et al. (2012) also described in their work that Ni is likely to be found in particles between 50 and 100 nm. Ni also presented an increase with engine speed for most of the tests. Regarding PM sizes, Ni is well distributed between all sizes, showing 33.5, 30.7, 27.7, and 8.5% for coarse particles, fine particles, ultrafine particles, and nanoparticles, respectively (SM 6).

Lead presented the highest emission values among elements for B5, B10, and B15, with a significant reduction when B20 fuel was used. The Pb emissions are distributed between coarse (43.3%), fine (25.0%), and ultrafine (29.7%) particles. Monaci et al. (2000) and Weckwerth (2001) described in their works that the presence of Pb is not common in diesel fuel, but in the soot from burning fuel, Pb is commonly quantified (SM 7).

Vanadium presented different results in comparison to other elements, becoming the exception of this research, with an increased emission with the biodiesel content. 75.2% of V emissions were concentrated in coarse particles and 23.0% in ultrafine particles. Vanadium was found in nanoparticles to a minor extent only in B5 emissions. Sanderson et al. (2014) reported that V is present in abundance in ultrafine particles in diesel. Miller et al. (2007) reported that V is a characteristic metal from combustion processes in general. These researchers add that V is naturally present in the lubricating oil and its presence in the PM is indicative of it. Probably, the biodiesel content has a direct influence on density and viscosity, increasing both properties, resulting in a poor fuel atomization, and forming large droplets with large jet penetration. This also can wash away the lube film increasing the lube oil consumption, forming large particles. So, attention must be paid to the presence of V in the lubricant oil and its effect on the emissions. It is likely that the lubricant oil formulation should be adjusted to minimize emissions, as stated by Mayer et al. (2012) in an extended study involving nanoparticles by diesel engines (SM 8).

Zinc concentration values showed a reduction with the biodiesel content for tests at 700 and 1000 rpm, but an increase at 1500 rpm. Almost half of the emissions are concentrated in the

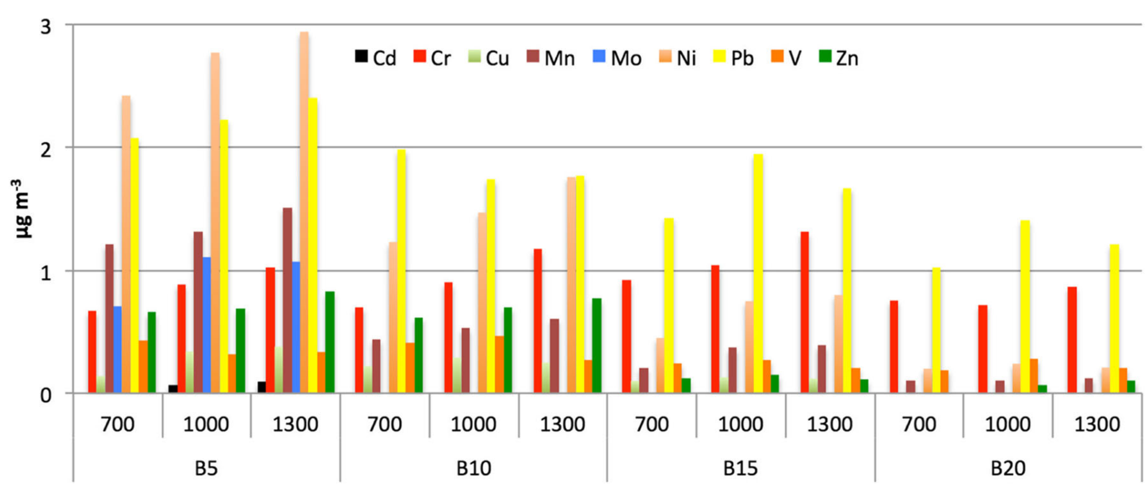

Fig. 4 Results for the emissions of ultrafine particles for B5, B10, B15, and B20 in different engine speeds (700, 1000, and 1300 rpm) for each metal

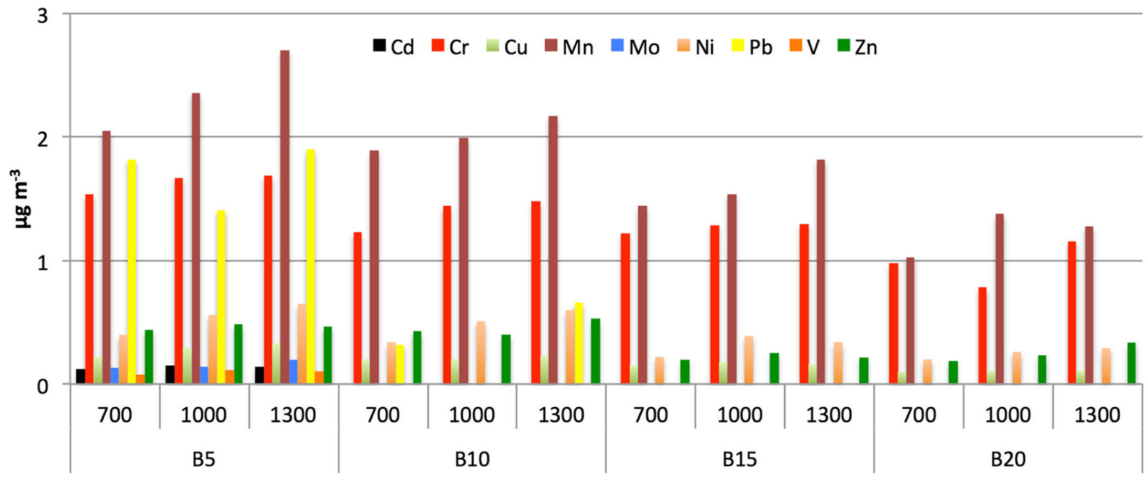

Fig. 5 Results for the emissions of nanoparticles for B5, B10, B15, and B20 in different engine speeds (700, 1000, and 1300 rpm) for each metal

coarse particles, and the other half are well distributed in fine particles, ultrafine particles, and nanoparticles (SM 9).

To understand the interrelationship between the emissions, a multivariate statistical analysis was done and the results are presented in the form of a dendrogram, combining all variables: fuel, metal, particle size, and engine speed. To perform this type of analysis, the R language (Core Team 2016) was used.

From Fig. 6, it is possible to observe that Cr, Mn, and Ni exhibit the highest concentration for all tests and Mn and Ni showed the greatest variability. The engine has several steel components and different types of steel, such as austenitic, ferrite, and carbide steels, and Ni, Mn, and Cr are present in all of these steels.

Analyzing the correlation between the metal elements presented in Fig. 7, it is possible to observe that Zn and V have the highest (100) positive correlation and possibly the same origin during the combustion process. Also, other strong correlations (≥ 75) were observed between Cr-Mn, Cd-Cr, Cd-Mo, Cu-V, Cu-Zn, Cu-Mo, and Cu-Cd. Several median correlations (between 25 and 50) were observed between all elements except between Pb-Mn, Pb-Cr, Pb-Ni, Ni-Cr, and Ni-Mn. Regarding biodiesel content, it is possible to identify an emission reduction in this order: Ni > Mn > Cr > Cd > V = Zn

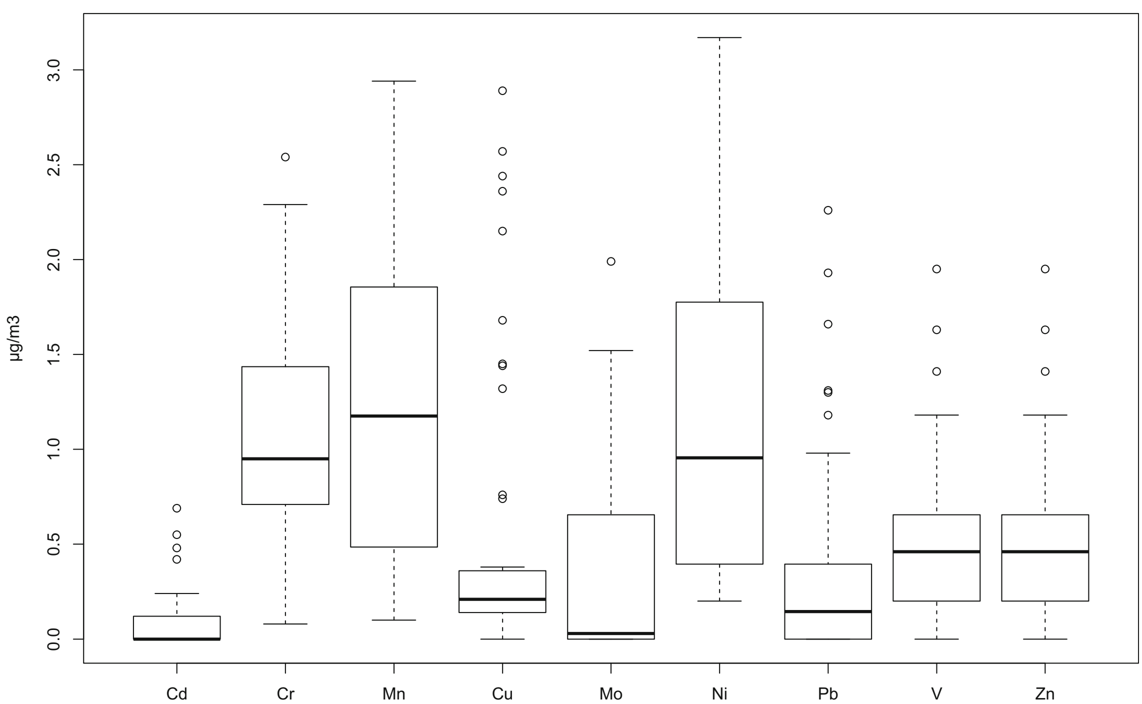

Fig. 6 Box plot of all elements grouped for all biodiesel blends and engine speeds

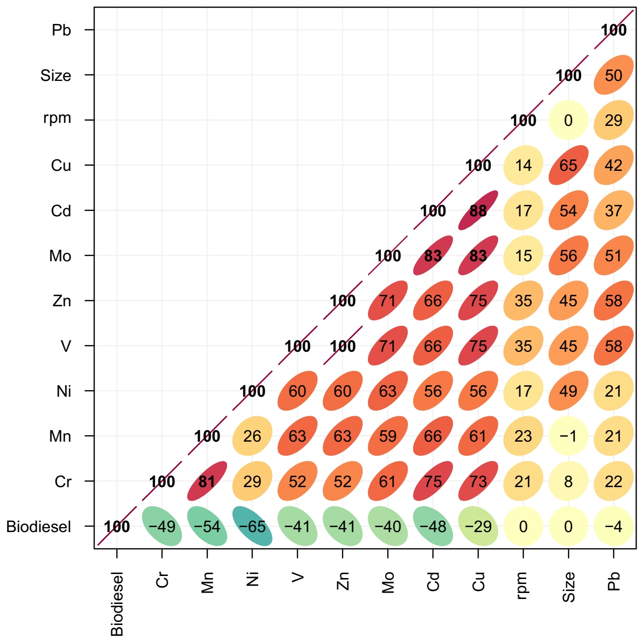

Fig. 7 Correlation matrix of all elements grouped for all biodiesel blends and engine speeds

>Mo > Cu >Pb. The engine speed is responsible for the increase in the following order: Zn = V > Pb > Mn > Cr > Cd = Ni > Mo > Cu. It is possible to identify that increasing the particle size the emissions increase as follow: Cu > Mo > Cd > Pb > Ni > Zn = V > Cr > Mn. No correlation was observed between particle size, biodiesel content, and engine speed.

The 3D dendrogram of Fig. 8 represents 77.26% of all data with three clusters. It is a way to reduce the data dimensionality and identify correlation between metal emissions. The lower the horizontal lines connecting the metals, the greater the correlation between the emissions. The dendrogram separated the data into three blocks. It is possible to visualize that Ni has a low correlation with other metals and probably has a different source compared to the other elements. It was also possible to see that Cr and Mn originate from the same source (different from the former) during combustion and a group composed by Cd, Mo, Pb, Zn, V, and Cu originates from another source. The lower the linkage of a group (e.g., Zn-V), the stronger is the correlation between data.

Conclusions

The obtained results can be a subsidy for Brazilian and international environmental agencies to better study the subject and to propose limits for vehicular emissions of metals in the particulate material and also for ambient air.

There was a gradual and significant reduction in the emission of metals during the addition of biodiesel in diesel, in a less extent for Pb. Nickel data showed that this element has a different source than the other metals and other possible similar sources are indicated for Cr-Mn, Cd-Mo-Pb, and Zn-V-Pb.

The increase of engine speed also indicates an increase in emissions of metals in the following order: Zn = V > Pb > Mn > Cr > Cd = Ni > Mo > Cu.

The main metals found in nanoparticles were Cr and Mn for all biodiesel content and Pb in B5.

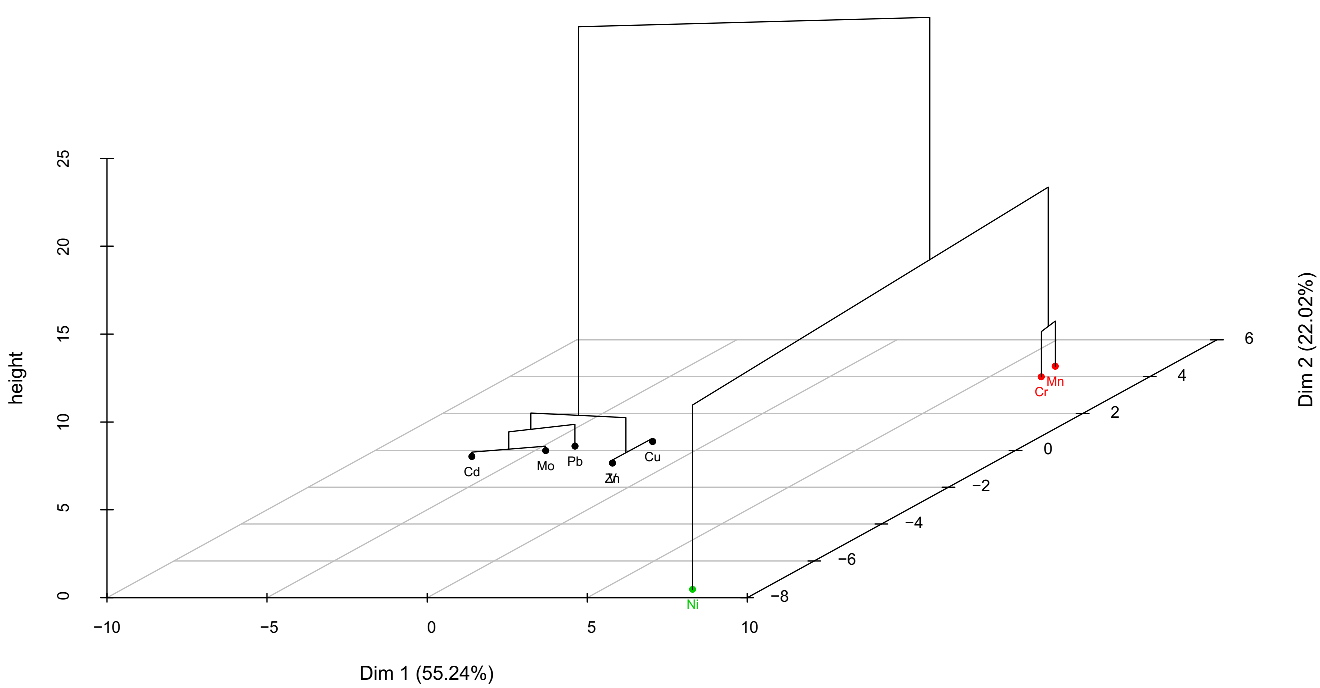

Fig. 8 3D dendogram of all elements grouped for all biodiesel blends and engine speeds

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