Possible influence of shipping emissions on metals in size-segregated particulate matter in Guanabara Bay (Rio de Janeiro, Brazil)

Renata S. Silveira · Sergio M. Corrêa · Newton de M. Neto

Abstract In the world of growing maritime fleets, ships powered by fossil fuels are being widely used that are responsible for atmospheric emissions such as particulate matter (PM). When inhaled, these can cause serious injury to the body and affect internal organs, because the particle size is on a tiny scale. The International Convention for the Prevention of Pollution from Ships (MARPOL) regulates the standards for emissions from marine diesel engines. However, although they pose risks to human health and the environment, the metals present in PM are not covered by Brazilian national current legislation. This study is based on the results of sampling of PM in the atmosphere of Guanabara Bay, Rio de Janeiro, Brazil, by means of the MOUDI cascade impactor, followed by acid opening of the collected PM and subsequent chemical analysis by ICP-MS for the determination of Ba, Ca, Cd, Co, Cu, Cr, Fe, Mg, Mn, Ni, Pb, V, and Zn. In coarse particles, the mean values ranged from 0.11 ng m^{-3} for Ba to 24.9 ng m^{-3} for Fe; in fine particles, from 0.07 ng m^{-3} for Co to 25.0 ng m^{-3} for Fe; and in ultrafine particles, from 0.11 ng m^{-3} for Ba to 9.71 ng m^{-3} for Fe. Finally, the nanoparticles (Ba and Ca) were not detected and the maximum value obtained was 5.32 ng m^{-3} for Mn.

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Introduction

Ships are widely recognized as being air polluters and an important source of urban pollution in ports; their transport over long distances affects the air quality of the land-based population. In the case of Brazil, most international freight is transported by sea, and the fact that the ships depend almost exclusively on fossil fuels has led to an increase in the emissions of atmospheric pollutants.

The health hazard posed by shipping is often overlooked when compared with land mobile services and fixed sources of energy. However, it includes activities such as construction, maintenance, disassembly, painting, hull cleaning, and paint removal and, above all, it should be noted that its energy matrix is based on heavy diesel oil with a high sulfur content, which is highly polluting. Prior to the application

of International Maritime Organization regulations (IMO, 2020), the sulfur content limit of fuels used on board ships was 3.5% w/w outside of Emission Control Areas (ECAs), which was considered a high content, compared to the updated limit, whose value is 0.50% w/w. As for ECAs, the default value (already established in 2015) of 0.1% was not changed (Contini & Merico, 2021).

Gases and particulate matter (PM) from diesel combustion contain toxic substances that are harmful to health, the environment, and the global atmosphere. These substances include metals that are responsible for a number of human diseases and emissions can have both a local and global impact.

The International Convention for the Prevention of Pollution from Ships (MARPOL, 1983) sets out the standards for the level of emissions from marine diesel engines and other technical devices in Annex VI (Prevention of Pollution from Ships − 2005). However, the metal content of their emissions from this source of pollution is unregulated.

The Convention on Long-Range Transboundary Air Pollution (CLRTAP) of 1979 of the United Nations Economic Commission for Europe (UNECE, 1979) is a regional treaty signed by 51 member states in the Northern Hemisphere (North America, Europe, and Asia). The objective of its protocol on metals is to reduce and control anthropogenic emissions of Pb, Cd, and Hg into the atmosphere by laying down guiding principles. According to this protocol, when metals are transported across international borders, their emissions can cause damage to ecosystems of environmental and economic importance, as well as having a harmful effect on human health.

The parameters regulated by current Brazilian environmental legislation are Total Suspended Particles (PTS), PM_{10} (inhaled particles), $PM_{2.5}$ (breathable particles), smoke, SO_2, CO, O_3, NO_2, and Pb (CONAMA, 2018). It is noteworthy that the atmospheric parameters $PM_{2.5}$ and Pb were not included in the old resolution. However, Pb should only be monitored if stipulated by the local environmental agency. Therefore, in Brazil, there is a lack of a national air quality monitoring plan that includes reference values of metals in the atmosphere.

Another important fact, which is not covered by the legislation, is the differentiated distribution of compounds with regard to particle size. In general, the most dangerous compounds are usually found in the small particles, where they cause greater damage and run the risk of being lodged in the deeper vital parts of the respiratory tract. As well as this, the small particles can be transported over greater distances and persist for long periods of time.

Maritime transport is essentially dependent on energy from petroleum products. If it continues to expand in the coming years, with the growth of freight and the increase of oil exploration (offshore), its emission of these pollutants is likely to increase, and there will definitely be pressures from society to take measures to address this problem.

The International Maritime Organization (IMO) is an international body that regulates maritime affairs on a global scale and has carried out several studies to understand the nature of the emissions from ships. It is a specialized agency of the United Nations and currently has 174 member states, including almost all the landlocked countries. To be effective, any measures to reduce emissions from shipping must be taken at an international level.

The main role of the IMO is to establish a regulatory framework for the shipping industry that is effective, universally adopted, and can be implemented through the national legislation of member states. Initially, IMO was mainly responsible for ensuring the safety of ships and seafarers, but now, its attention is increasingly concentrated on environmental protection and ensuring that ships do not pollute the oceans and atmosphere.

According to the UN (2020), around 80% of global trade is transported by sea; this is essential for economic growth, as it plays a vital role in spreading wealth and raising people's standard of living around the world.

With the growth of global trade, the demand for shipping services is also expected to increase, as well as the number of ships. According to Paulauskas et al. (2020), at the beginning of 2019, the entire world fleet consisted of 95,402 ships. In addition to the global trading activities of shipping, there is a demand for maritime tours which has led to the construction of cruise ships, capable of carrying thousands of passengers across the sea.

Only the signatory parties can enforce the regulations, but even a ship flying the flag of a non-signatory party is required to comply with them, including the requirements laid down for construction, when sailing in the waters of a signatory party. Annex VI is responsible

for regulating the degree of air pollution from ships and includes clauses designed to control ozone-depleting substances (VOCs and NOx). At large distances from the emissions, the excess of NO_2 due to ships could enhance the O_3 production at ground level even if, at local scale, a depletion of O_3 due to NO releases is often observed (Contini & Merico, 2021). These pollutants are hazardous because they can cause several local problems, especially with regard to air quality, which has a direct impact on public health.

This study has been conducted in collaboration with other research on the quantification of metals found in emissions from ships in Guanabara Bay, located in Rio de Janeiro, Brazil, by means of the MOUDI particle impactor (Micro-Orifice Uniform Deposite Impactor) for sampling. Although there are several studies on metal emissions from maritime transport, studies with multi-stage impactors are more limited (Gregoris et al., 2021; Mifka et al., 2021). The present work seeks to expand the information on the impact of maritime transport for measurements segregated by sizes of metals and to assist public policymaking for air quality with regard to ships, as their emissions need to be regulated at local, regional, and international levels.

There are some publications on ship emissions and their effects, such as the study by Corbett et al. (2007) who investigated ambient PM standards and concentrations for oceangoing ships and their health effects; they concluded that 60,000 annual deaths can be attributed to pollution sources.

According to Contini and Merico (2021), air pollutant emissions from the maritime transport sector contribute to the degradation of air quality in port cities, representing an emerging risk to the health of the coastal population. Emissions from ships are a matter of concern for the management of urban air quality in many ports. The adverse effects of maritime transport on the environment are mainly concentrated on major ports, such as Shanghai, Rotterdam, and Hamburg, and waterways such as the Suez and Panama Canals and the Straits of Gibraltar.

Although the IMO has made serious attempts to reduce emissions from ships, there is no specific legislation for the metals that can be found in these polluting sources. Hence, there is a need to carry out a diagnosis of the atmospheric pollution caused by ships and in particular, their effects, on the health of coastal communities, assistance should also be provided, through sampling techniques, methods for preparing and extracting samples, and analytical procedures for the detection and quantification of organic and inorganic compounds, to enable states to regulate the problem.

Similar works on ship emissions have been published such as the following: Ytreberg et al. (2021), Tang et al. (2020), Zhang et al. (2019), Tao et al. (2017), Simonsen et al. (2019), and Eckhardt et al. (2013), among others. However, many of these publications are focused on China, the USA, and Europe, which means there is a lack of data for the situation in Brazil, especially with regard to Guanabara Bay and its densely populated surroundings where there is a constant flow of ships.

The number of existing studies on the contribution of ships to the emission of gaseous pollutants SO_2 and NOx is greater than the number of studies on the presence of metals in PM, which makes these pollutants a matter of interest for IMO regulation. While regulation of the emission of gaseous pollutants is important for mitigation strategies, the use of low sulfur fuels will not bring significant changes to total metals and PAHs in the gaseous and particulate phase (Contini & Merico, 2021). Thus, studies that aim to characterize the emissions of metals and PAHs are important for the debate on the regulation of these pollutants, especially in large urban centers and port cities due to the risk to the health of the population.

Furthermore, the contribution of ship emissions to the concentration of metals in PM in the city of Rio de Janeiro (Brazil) is still under debate and needs to be addressed for better understanding and national regulation. This work presents for the first time the quantification of metals in PM in Guanabara Bay (Rio de Janeiro, Brazil) considering different particle size ranges and investigating possible sources.

The distribution of metals in PM was categorized in four size ranges (coarse, fine, ultrafine, and nano) and measured over a period of a year, as well as the concentration of metals in marine diesel oil. The data obtained were handled statistically in a descriptive and multivariate manner.

Methodology

Area of study

Guanabara Bay is an oceanic bay located in the State of Rio de Janeiro, in southeastern Brazil, latitude 22°54′0″ S and longitude 43°12′0″ W, with 381 km².

It is widely used for the mooring and anchoring of vessels, and brings together 16 municipalities in its surrounding area, with a population of more than 12 million inhabitants (IBGE, 2019).

It is considered to be one of the most beautiful and sheltered bays in the world and is surrounded by a mountain range, notably the Sugar Loaf and Corcovado Mountains. However, it is an environment susceptible to the accumulation of pollutants because of its very peculiar conditions. Figure 1 shows Guanabara Bay on the map and the point marked in red is the sampling site.

Guanabara Bay shelters naval bases, shipyards, and a large number of ferries, fishing boats, and yachts, as well as ports and terminals, where thousands of ships dock annually. The Port of Niterói, the Port of Rio de Janeiro, the Ilha d'Água Terminal (Almirante Tamandaré), the Ilha Redonda Terminal, and the Guanabara Bay LNG Flexible Terminal should also be mentioned. According to Companhia Docas do Rio de Janeiro (CDRJ, 2022a), the Port of Rio de Janeiro has an operating area of 1 million m^2 and handled 220,354 passengers in 2020 and 2019,

before the COVID-19 pandemic, the movement was 363,659 passengers (CDRJ, 2022b) In addition, it handled 8,161,282 tons of cargo in 2020 (CDRJ, 2022c). The Port of Niterói has an operational area of 21,900 m^2 and handled 84,497 tons of cargo in 2020 (CDRJ, 2022d). Figure 2 shows Guanabara Bay on a nautical chart and includes an illustration of the number of ships present.

Data collection

A total of 57 samples were collected between October 2019 and January 2021, by means of an MSP MOUDI 120R cascade impactor with 10 rotating stages. This was carried out over a period of 24 h on working days and at weekends, to limit the influence of pollution from urban road traffic on the Rio-Niterói Bridge and from avenues in the town center of Rio de Janeiro. Sampling took place at a constant flow rate of 30 L min^{-1}. An average sample percentage between 7 and 10% per month was collected.

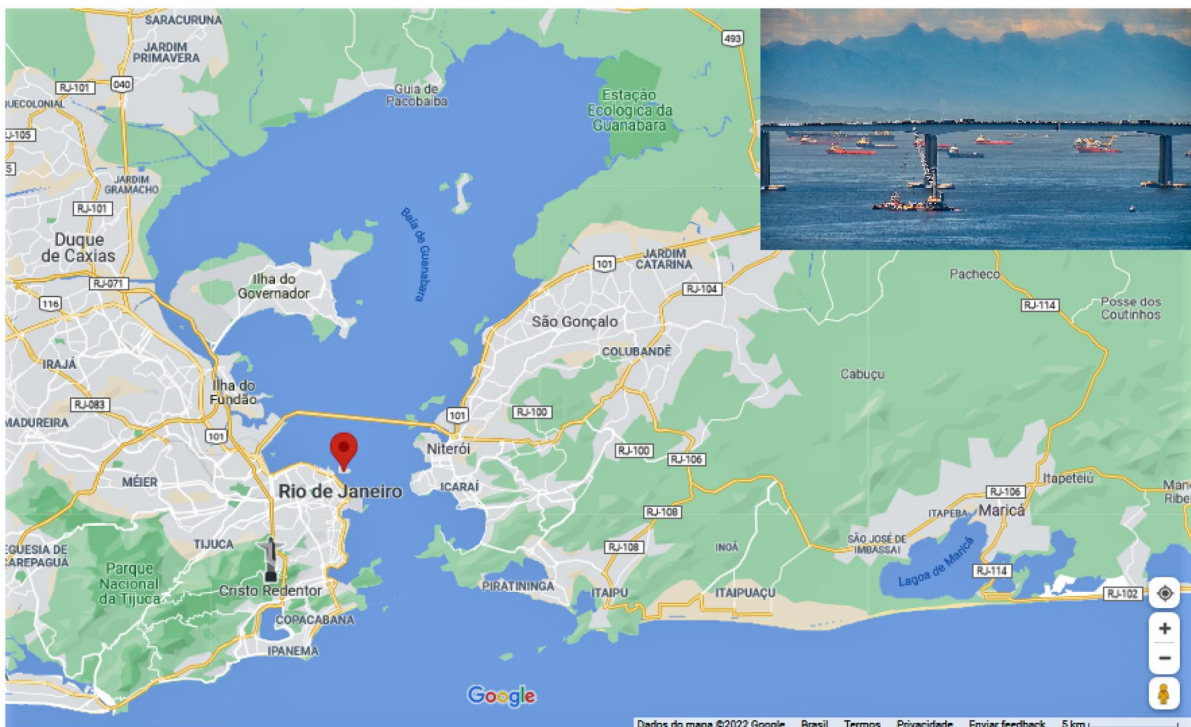The duration of the sampling was adjusted for some preliminary samples which were collected over

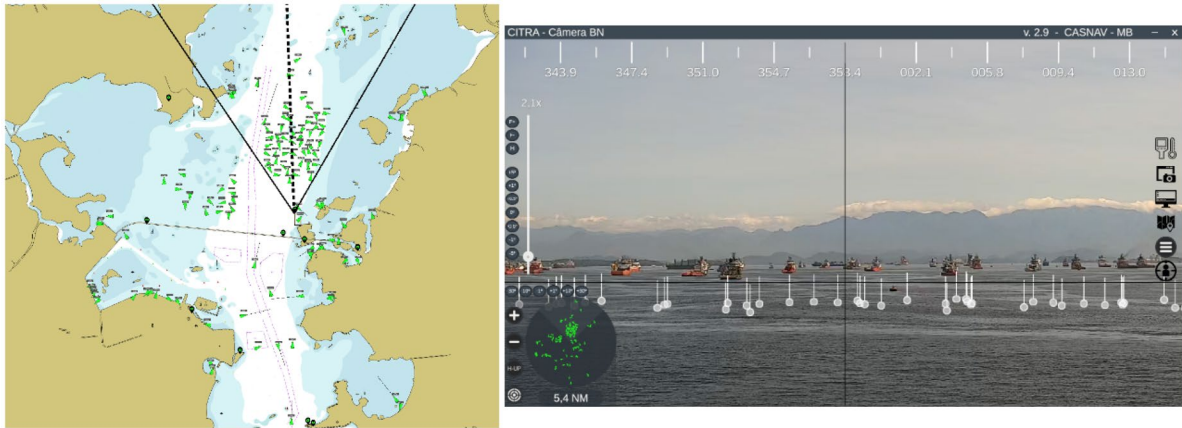**Fig. 1** Map of Guanabara Bay, Rio de Janeiro, Brazil. Source: Google Maps, 2022

Fig. 2 Nautical chart with some boats in Guanabara Bay, Rio de Janeiro, Brazil. Source: CITRA (2021)

a period of 24 and 48 h but, after the extraction and chemical analysis, it was noted that a duration of 24 h was sufficient because of the analytical limit of quantification (LOQ) of the method, at least for the elements studied in this work.

In each stage of the impactor, hydrophobic polytetrafluoroethylene (PTFE) membranes were used with 0.22 μm of porosity and 47 mm in diameter (Filtrilo MFPTFE-4722). After the sampling, the membranes were stored in 60 × 15 mm Petri PS plates, grouped into four particle size ranges (coarse, fine, ultrafine, and nanoparticles). Particles from 1.8 to 10 μm were grouped as coarse particulate matter (PMC). Particles from 560 nm to 1.8 μm were classified as fine particulate matter (PMF). Particles from 100 to 560 nm were included in the ultrafine particulate matter (PMUF) classification, while particles below 100 nm were categorized as nanometric particulate matter (PMN). The plates were wrapped in aluminum foil and placed in a freezer at −20 °C until further extraction and chemical analysis, in accordance with the methodology outlined in a previous publication (Rocha & Corrêa, 2018).

On each sampling day, other variables were collected for a multivariate study. Meteorological data were obtained from the Niteroi Station of the National Institute of Meteorology (temperature, relative humidity, atmospheric pressure, rainfall, wind direction, and speed). The calculation of the number of vessels was based on real-time marine vessel tracking available in Marine Traffic. The data from the Air Quality Monitoring Program (MonitorAR Rio) in the town center

of Rio de Janeiro provided air quality values, such as carbon monoxide (CO) and ozone (O_3). Data were also consulted on the number of vehicles that monthly cross the Rio-Niterói Bridge and on two nearby roads with heavy traffic (Avenida Primeiro de Março and Avenida Rio Branco). It is worth noting that, in the period of collection, (pre-pandemic of COVID-19), the Port of Rio de Janeiro experienced a rise in freight handling of approximately 5%, which denotes intense ship traffic (ANTAQ, 2019).

The samples were collected on Ilha das Cobras, (latitude 22°89′72.5″ S and longitude 43°17′40.3″ W), that is, inside Guanabara Bay, as indicated by the red marker in Fig. 1.

Sample extraction

One of the most widely used metal extraction methods in the literature is the U.S.EPA IO-3.5 method, which describes the selection, preparation, and extraction of filters used to collect PM and was chosen in this work because of its wide acceptance (U.S.EPA, 1999). According to Ventura et al. (2017), the method meets all the validation criteria established by EURACHEM (2014).

Each of the membranes of MOUDI was placed in 50 mL glass vials and identified according to the size range (PMC, PMF, PMUF, PMN). Ten milliliters of distilled water and 8 mL of HNO_3 (Merck Suprapur) were then added to each flask. After reaching boiling point, it was left for another 1 h. Then, the flasks were cooled with ice water to about 10 °C. Ten milliliters

of dichloromethane (Sigma-Aldrich GC grade) was then added and the mixture was placed in an ultrasound bath with ice water for 30 min. After decanting for about 2 h, the organic and inorganic liquids were separated and put in a separatory funnel. The organic liquid was stored in 10 mL vials and reserved for later PAH analysis. The inorganic liquid was transferred to clean 50 mL flasks and allowed to dry on a hot plate. Then, 10 mL of 3 mol L^{-1} HNO_3 was added and transferred to 15 mL vials.

Chemical analyses

The resulting solution was analyzed by ICP-MS (Perkin Elmer ELAN 6000, USA). The accuracy of the methodology was determined from the analysis of certified samples of particulate material (NIST SRM 1648a). A chemical analysis was conducted by ICP-MS with the samples preheated to 80 °C. A power of 1200 W was used at 27 MHz, plasma flow of 12.0 L min^{-1}, 0.60 L min^{-1} of auxiliary gas, 1.00 L min^{-1} in the nebulizer, sample aspiration flow of 0.5 mL min^{-1}, acquisition time of 1 s, and dwell time of 200 ms.

The results were obtained from the average of 5 readings of each sample for the determination of Ba, Ca, Cd, Co, Cu, Cr, Fe, Mg, Mn, Ni, Pb, V, and Zn. The analytical 7-point curves in triplicate were performed with the multielement standard solution and the limits of quantification obtained were 0.310 µg L^{-1} for Ba, 12.10 µg L^{-1} for Ca, 0.092 µg L^{-1} for Cd, 0.018 µg L^{-1} for Co, 0.060 µg L^{-1} for Cu, 0.380 µg L^{-1} for Cr, 8.93 µg L^{-1} for Fe, 0.360 µg L^{-1} for Mg, 0.320 µg L^{-1} for Mn, 0.210 µg L^{-1} for Ni, 0.067 µg L^{-1} for Pb, 0.018 µg L^{-1} for V, and 2.25 µg L^{-1} for Zn.

Marine diesel from a tanker, a tugboat, and a frigate was also analyzed, to check if metals were present in the fuel. The same metals as the ambient air samples were determined, except for Co. The limits of quantification obtained were 0.012 mg kg^{-1} for Ba, 0.050 mg kg^{-1} for Ca, 0.016 mg kg^{-1} for Cd, 0.040 mg kg^{-1} for Cr, 0.190 mg kg^{-1} for Cu, 0.040 mg kg^{-1} for Fe, 0.035 mg kg^{-1} for Mg, 0.035 mg kg^{-1} for Mn, 0.065 mg kg^{-1} for Ni, 0.060 mg kg^{-1} for Pb, 0.020 mg kg^{-1} for V, and 0.046 mg kg^{-1} for Zn.

Results and discussion

The harmful effects of PM emissions vary according to their size (Kreyling et al., 2006), morphology (Dunnick, 2015), and chemical composition (Pöschl, 2005).The percentages of the total analyzed metals with regard to the composition of the collected PM, on the basis of the particle sizes, were 33% PMC, 32% PMF, 22% PMUF, and 13% PMN. Table 1 shows the average results of the metal concentrations in ambient air.

Table 1 Mean concentrations of metals in ambient air and in the fuel used on ships

Metal	Ambient air (ng m^{-3})						Fuel (mg kg^{-1})		
	This study				Ntziachristos et al. (2007)	Lough et al. (2005)	This study		
	PMC	PMF	PMUF	PMN	California, US ships	Wisconsin, US vehicles	Tank ship	Tug ship	Frigate
Ba	0.108	0.107	0.106	-	~1–2.00	0.73	15.01	9.39	1.61
Ca	5.648	4.018	4.630	-	~6.00	-	18.62	21.68	15.08
Cd	0.831	0.896	0.922	1.053	-	0.013	0.53	0.39	0.59
Co	0.314	0.066	0.558	0.101	-	0.98	-	-	-
Cr	0.774	0.564	1.000	1.155	-	2.1	1.47	1.28	0.74
Cu	2.140	2.524	2.807	2.695	~1–2.00	6.1	1.03	1.22	0.60
Fe	24.86	25.00	9.709	2.368	35.00	8.0	8.50	7.18	6.49
Mg	0.73	0.64	0.42	0.16	-	25.0	9.46	8.39	6.27
Mn	2.313	3.228	3.693	5.322	-	0.52	0.91	1.06	0.59
Ni	0.695	0.735	1.189	1.261	-	-	0.09	<LQ	<LQ
Pb	0.98	1.21	1.16	0.31	-	0.062	2.23	1.43	0.76
V	0.252	0.543	0.957	0.925	-	0.78	0.43	0.10	0.07
Zn	2.54	3.24	3.15	2.63	~1–2.00	3.2	12.09	9.86	7.60

According to Momenimovahed et al. (2021), it is the low-quality fuels used in the shipping industry that are responsible for significant amounts of air pollution worldwide. In most cases, the fuel used in marine engines outside Emission Control Areas is residual fuel, i.e., heavy or intermediate fuel oil with significant amounts of metals and a high sulfur content. It should be noted that the metals found most often in the fuels analyzed in this article were Fe, Ca, Mn, and Zn.

Agrawal et al. (2009) state that the transition metals V and Ni are robust markers for the combustion of heavy fuel oil in ships. According to Agrawal et al. (2009), the presence of V, Fe, and Ni in PM can be attributed to primary emissions from residual sources of oil, such as exhaust gas from ship engines. The compounds Ca and Zn are combined with lubricating oil and not with fuel (Mayer et al., 2010).

Pandolfi et al. (2011) point out that in the Straits of Gibraltar, the V/Ni ratio is 3. In the present article, high concentrations of Fe and Ni can be observed, but the concentration of V in ambient air is low, compared with what is found in the international literature, on the basis of the 57 samples taken on both on weekdays and at weekends. In this study, the values found were V/Ni = 0.36 for PMC, V/Ni = 0.73 for PMF, V/Ni = 0.80 for PMUF, and V/Ni = 0.73 for PMN. However, it should be remembered that the Straits of Gibraltar is one of the biggest bottlenecks in world shipping. Currently, it is estimated that around 90,000 vessz every year and that, on average, one vessel passes through every 6 min (Agency, 2009). This difference may be due to the type of fuel used by the vessels, given that the values found for V and Ni in the fuel are low in this study. The V/Ni ratio may also differ due to the presence of other sources with different fuels. Lower-than-expected and wind direction-dependent V/Ni ratios were also found in a European port in the study by Cesari et al. (2014). Even the Ni in the tugboat and frigate was below the limit of quantification. In our study, account must also be taken of the influence of other nearby sources, such as vehicles in the Metropolitan Region of Rio de Janeiro.

Statistical analysis

The first approach to the data obtained was to display the boxplots for each size range of the evaluated metals, as shown in Fig. 3. In order to equalize the graphs, a multiplier factor for Fe of 0.3 was used for coarse, fine, and ultrafine particles.
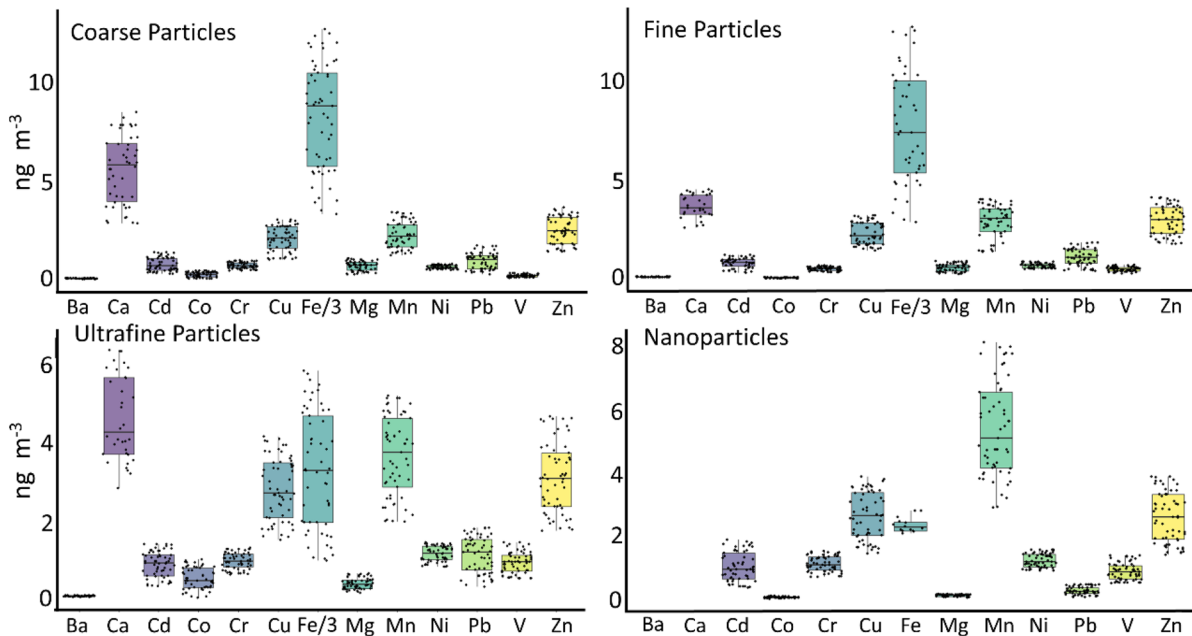

Fig. 3 Boxplot for all the samples divided into four sizes

The metals that had the highest concentrations were Fe in coarse, fine, and ultrafine particles and Mn in nanoparticles. Wang et al. (2013), in a study carried out of the atmosphere over the Northern Yellow Sea, found that Fe was the second most abundant trace metal after Al, with a concentration ranging from 326.5 to 2111 ng m^{-3}.

According to Gregoris et al. (2016), Fe and Zn were the most abundant metals among the atmospheric pollutants in the Venice lagoon. They also stated that Pb and Zn are traffic emission markers, but they also may be present in industrial emissions.

Figure 4 shows the average data for all the metals stratified by day of the week and the results show a small reduction at weekends. An average of 149 ships was observed on weekdays and an average of 131

ships at weekends and on holidays. The two-sample test for means (test Z) was carried out to confirm that weekdays and weekends are statistically different. The z_{test} value found was 3.45 and (the z_{test} value) is equal to 1.96 for the 95% confidence interval. As a calculated z_{test} is greater than a tabulated z_{test}, it can be said with 95% degree of certainty that the number of vessels on weekdays is statistically higher than at weekends.

It should be noted that, regardless of the particle size range, the concentration of metals in PM was lower at weekends than on weekdays.

Figure 5 shows the average values for the metals of the 57 samples and the hourly average data for the criteria pollutants (PM, CO, and O$_3$). In the case of O$_3$, the data corroborate the behavior observed by
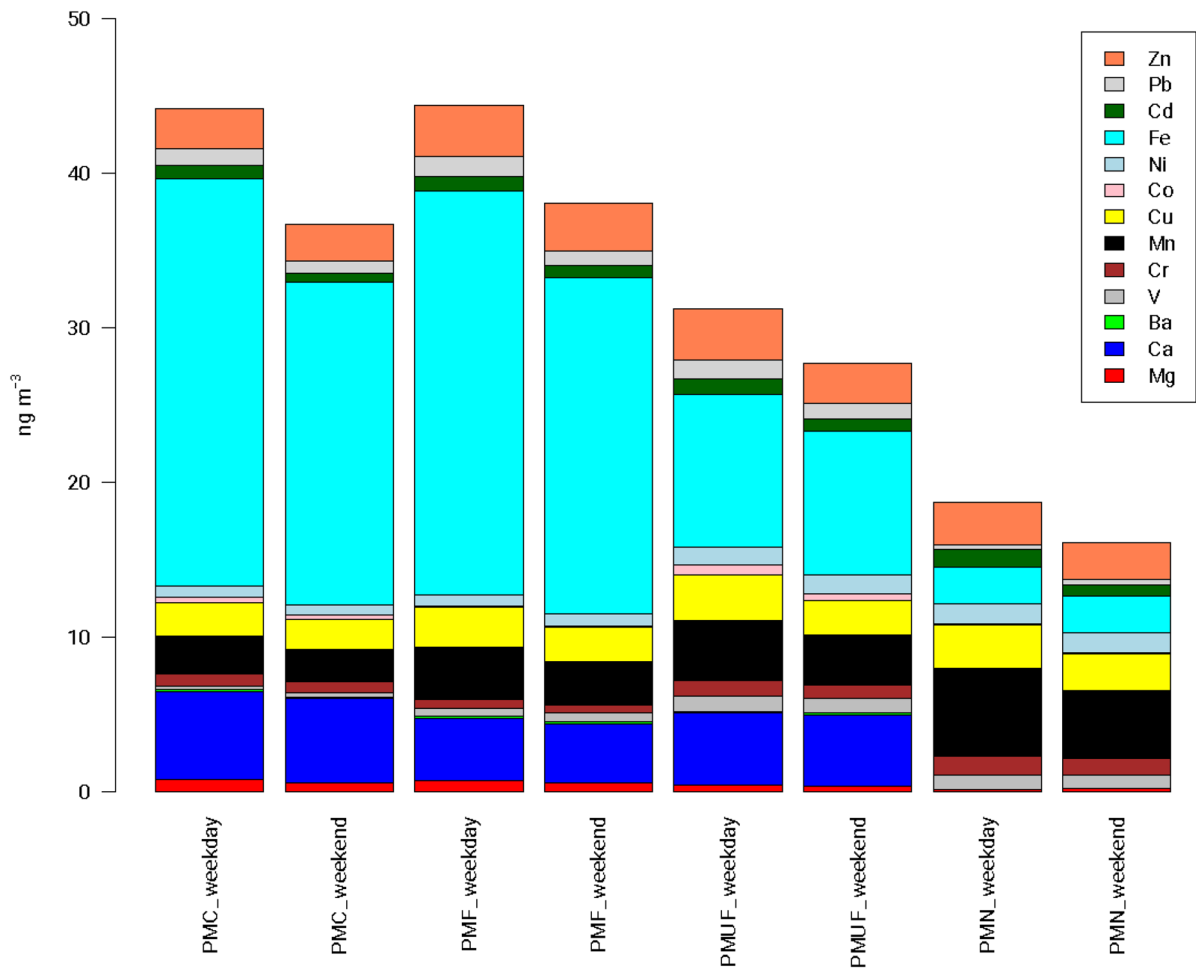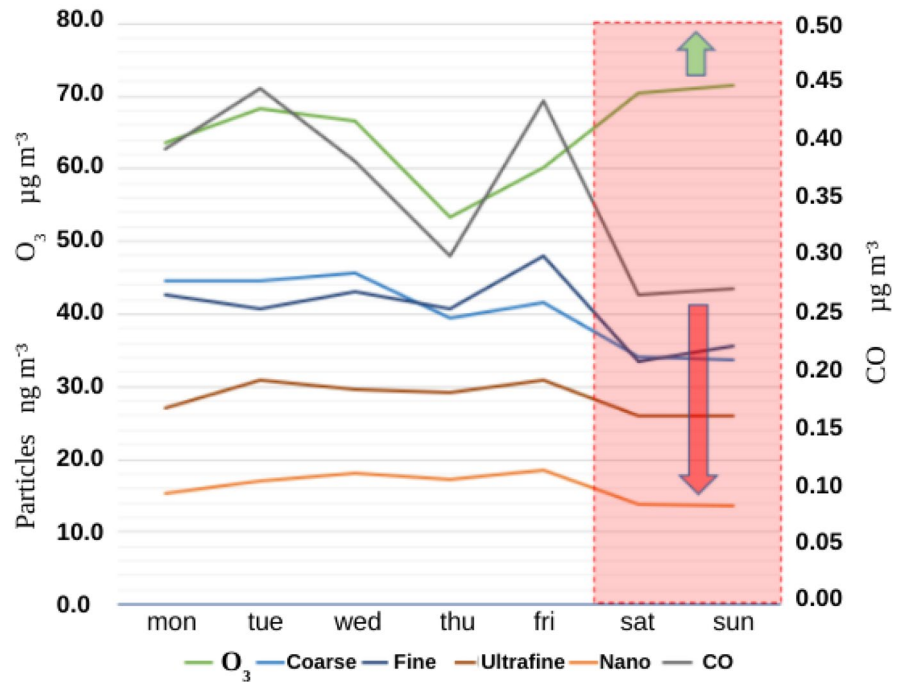

Fig. 4 PM distribution by weekday and weekend

Fig. 5 Data of O₃, CO, and PM by day of the week

Geraldino et al. (2017, 2020) for two districts of the city of Rio de Janeiro, where there is an increase in O₃ owing to the reduction of heavy vehicles, with a consequent reduction in NO, which reacts with O₃. A similar pattern for weekends can be observed for CO and PM.

In Fig. 6, the concentrations of metals found were grouped monthly, in accordance with the months in which there were collections, and contrasted with the average flow of ships, vehicles, and planes of each month, with data referring to Santos Dumont Airport, located near Guanabara Bay. The percentage of ships, vehicles, and planes is calculated according to the total number of each transport during the whole period considering the average of each month (October 2019–January 2021).

There was a drop in the amount of vehicular, shipping, and plane traffic during the months of March/April 2020, as a result of the pandemic, as well as the concentration of evaluated metals in the atmosphere. The relationship between the variables for the 4 size ranges was calculated by means of Pearson's correlation coefficient, as shown in Fig. 7.
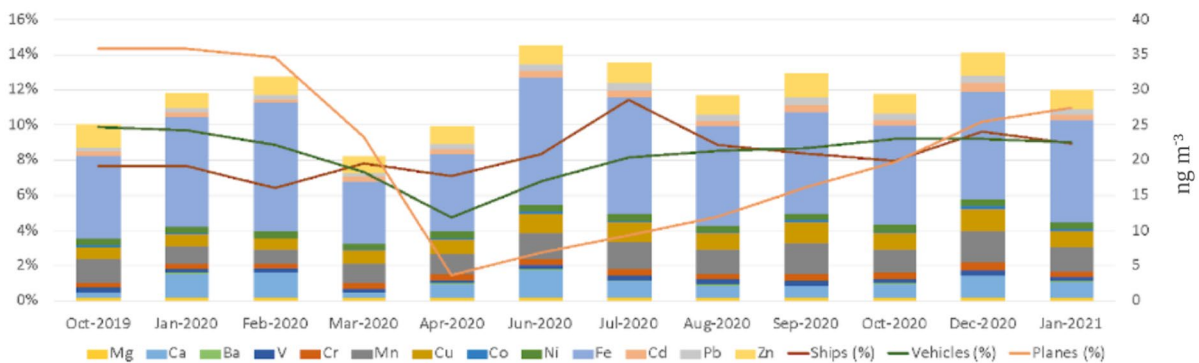

Fig. 6 Comparison of metal concentrations and the flow of ships, vehicles, and planes
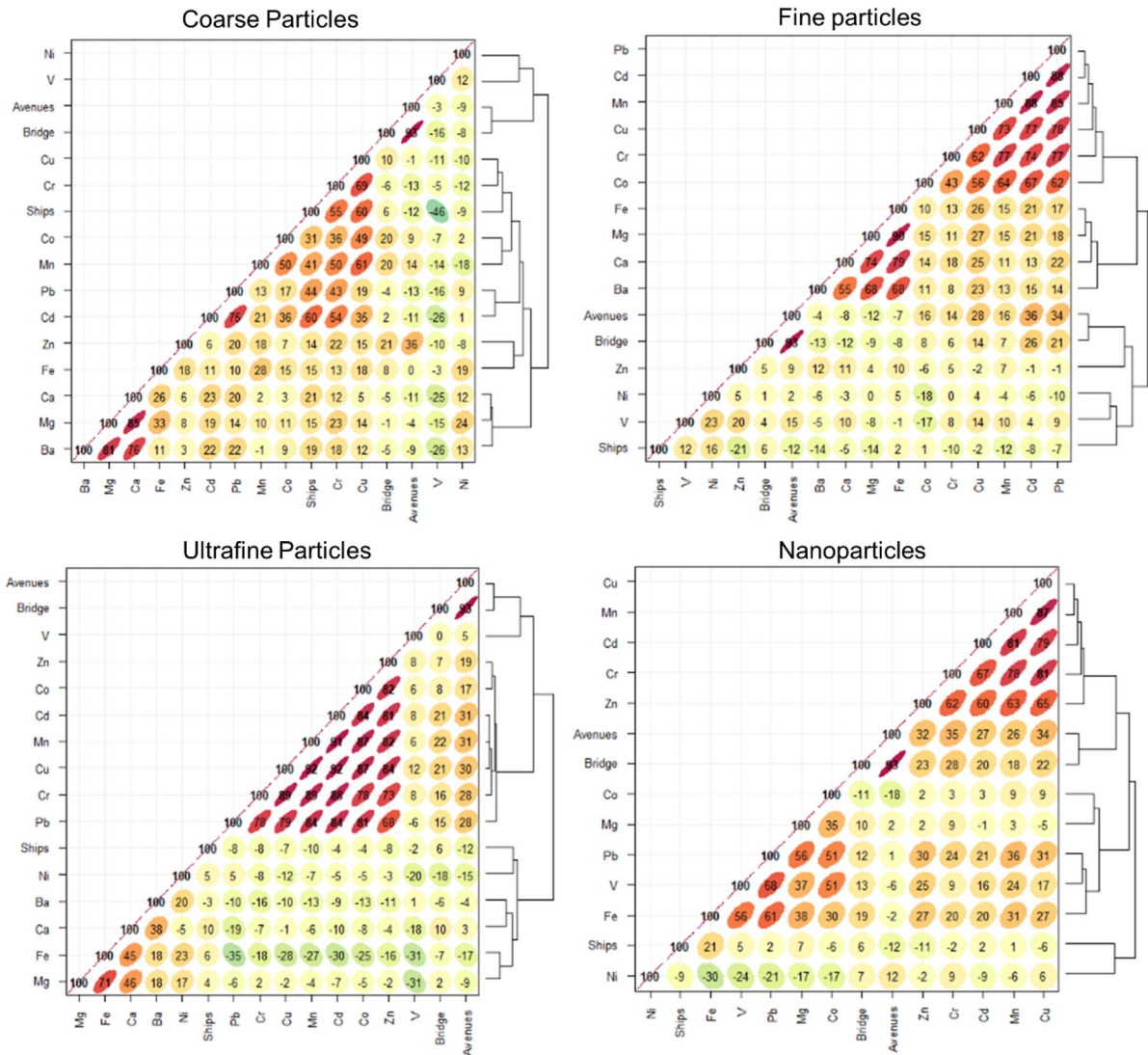
Fig. 7 Pearson's correlation matrices for the 4 PM sizes

In PMC and PMF, there is a high correlation between alkaline earths (Mg, Ca, and Ba), which suggests that these metals may have the same emitting source. Pb and Cd have close correlations for PMC, PMF, and PMUF, but less for PMN. In the case of the 4 PM size ranges, there is always a close correlation between the flow of vehicles on the Rio-Niterói Bridge and Rio Branco and Presidente Vargas avenues, as expected, as they are the main roads in the town center of Rio de Janeiro. In the 4 size ranges, there is also a close correlation between Cu, Cr, and Mn and also with Co, with the exception of PMN.

Other close correlations are also found for the PMC between Zn + Fe, Pb + Cd, and Ni + V, for the PMF between Mn + Fe, Pb + Cd, and Ni + V, for the PMUF between Fe + Mn + Ca, and for the PMN between Pb + V + Fe.

The next calculation was a principal component analysis (PCA), which makes a classification and works with a more cohesive dataset, as shown in Fig. 8. The following group was obtained for the first two dimensions obtained by the PCA classification; 37.1, 41.2, 47.8, and 42.6% for PMC, PMF, PMUF, and PMN, respectively.
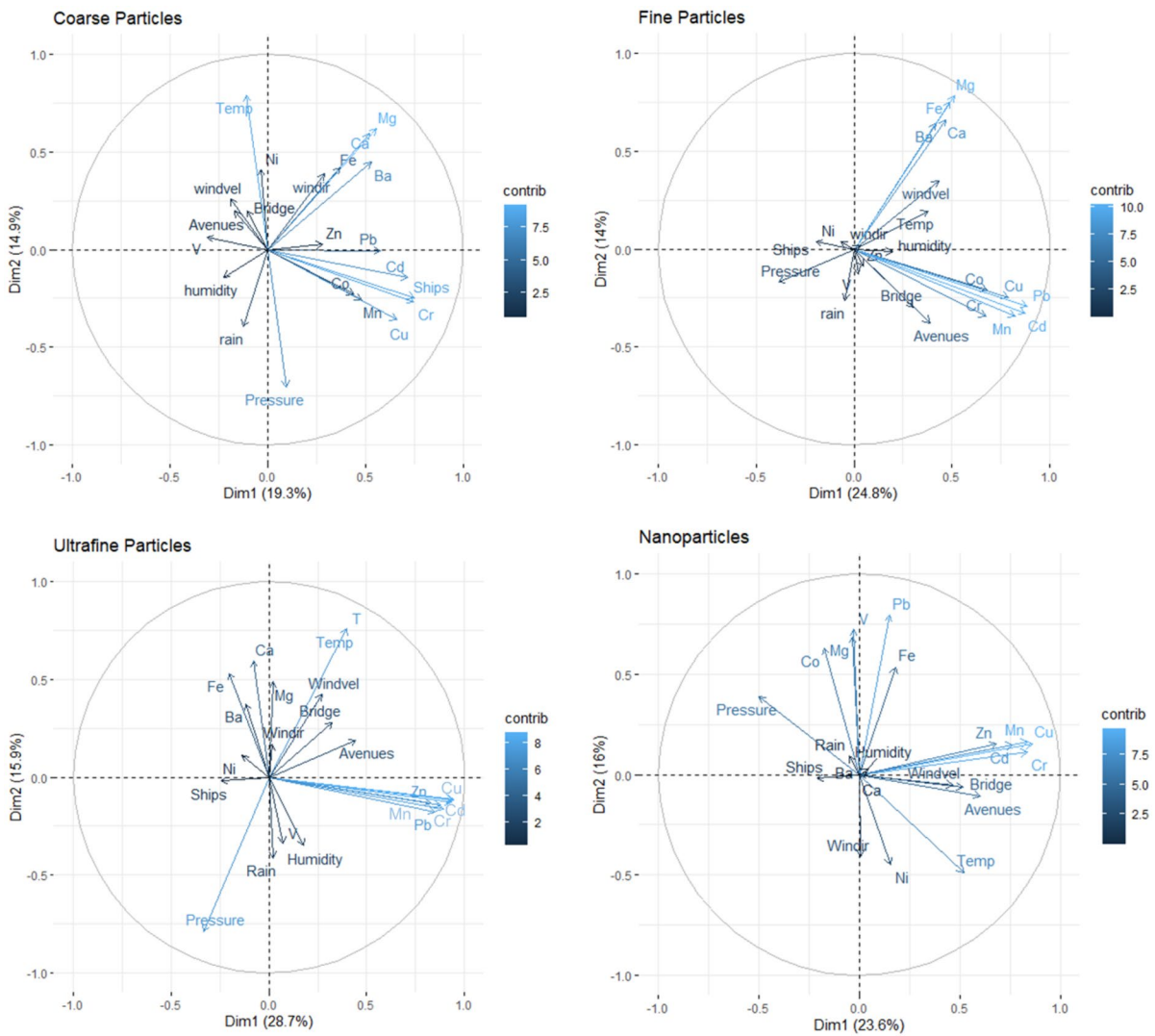
Fig. 8 Principal component analysis for the 4 PM sizes

Two sets of variables were observed for PMC, for example Ca + Mg + Ba + Fe + WD which suggests that these metals may originate in the soil and be transported by the wind. Another significant grouping occurs among Pb + Zn + Cd + Cr + Cu + Co + Mn, together with the flow of ships. This is a notable indication that these metals in the PMC might originate from shipping emissions. PMC, V, and Ni have no relationship with any other metal, nor with ships or traffic flow.

The same set Ca + Mg + Ba + Fe + WD was observed for PMF, which corroborates the view that these metals might originate in the soil and be transported by the wind. Another significant grouping is between Pb + Cd + Cr + Cu + Co + Mn but this time, they are not related to the flow of ships but to vehicles. Ni and V have little relationship with the other metals or Zn either. Shipping flow appears to have little correlation with all the metals evaluated for the PMF.

When the PMUF was assessed once again, the group formed of Pb + Zn + Cd + Cr + Cu + Co + Mn stood out, but did not have any relation to the flow of ships, or the group between Ca + Mg + Ba + Fe once again and the wind direction, which suggests it may have been transported from other regions. Likewise, V and Ni had results which were different from the others.
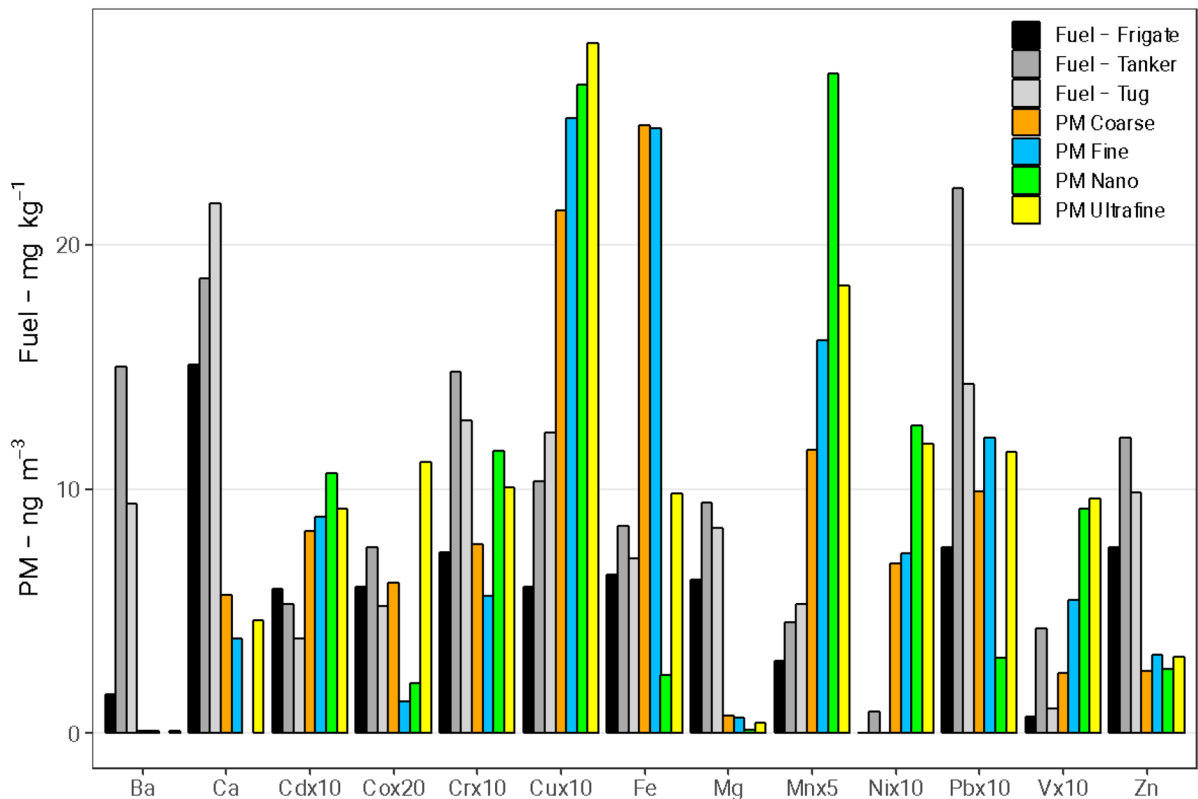
Fig. 9 Comparison between the concentration of metals in the atmosphere and the fuels used by ships

In the case of the PMN, the group that is found in the other PM sizes between Zn+Mn+Cd+Cu+Cr, there is a slight correlation with wind speed. In this size range, there is another group which is not observed in the others, such as the group between Mg+Co+V+Pb+Fe. In this PM size range, Ba and Ca do not correlate with the other variables and once again, Ni seems to be detached from all the other variables and is a metal that needs to have its source identified.

When all the PCAs are examined more comprehensively, it can be seen that PMC, PMF, and PMUF have a similar distribution of vectors, only the PMN has a different distribution and may have different sources.

As the sampling site was located in the center of the city of Rio de Janeiro, where there is a constant flow of light vehicles and buses, the Tukey test was conducted to check the effect of land mobile services on the results. This test was carried out (Fig. 9) to determine whether it would be necessary to separate the data from weekdays from that

of weekends, so that the data obtained from naval emissions could be correlated.

Tukey test was used to compare the samples collected between weekdays and weekends with a 95% confidence interval. The results indicated that only Cd with high certainty, and Cr and Mg (threshold) have a different behavioral pattern between weekends and weekdays for all the size ranges. In view of this, it was decided that the samples could be handled together for the study by comparing the results in the atmosphere with the results obtained from 3 types of fuel used by 3 ships of the Brazilian Navy, a frigate, a tanker, and a tugboat (as shown in Fig. 9).

According to Zhang et al. (2019), the fraction of the number of particles emitted by ships is directly proportional to the increase in marine traffic, but the particles tend to contain a lower V content. This is in compliance with the policy of the Domestic Emissions Control Area (DECA) (Transportation, 2019), which regulates sulfur oxide (SOx) and nitrogen oxide (NOx) emissions from ships in Shanghai.

Owing to the change from DECA 1.0 to DECA 2.0, the study by Yu et al. (2021) investigated the effect of marine fuel oil regulations on ambient air V and Ni concentrations on the basis of a 4-year (2017–2020) online measurement in Shanghai. They stated that both the DECA and IMO (2020) regulations, which restrict the use of sulfur in fuel oil by ships operating outside designated emission control areas, effectively reduced the V environment; this also applied to samples of shipping oil with a viscosity of 180 cSt from 2010 to 2020. However, the content of Ni is still supplemented by the desulfurized residual oils in use and particles emitted by ships off the coast of China.

In this study, it can be seen that the Ni content in the oils used in Brazil is lower than in the case of China, since in the tanker, the value found was 0.09 mg kg^{-1}. On the frigate and tugboat, the results obtained were below the detection limit. With regard to the ambient V, a maximum value of 0.957 ng m^{-3} was obtained in the ultrafine particles and 0.43 mg kg^{-1} in the fuel of the tanker.

Conclusion

This study is the first attempt to quantify the environmental impact of residual metals (V and Ni) from ship emissions in Guanabara Bay. Coarse, fine, ultrafine, and nano particles of V and Ni emitted by ships were quantified, but our findings suggest that, with regard to metals, they do not have a significant effect on the air quality of coastal areas. Moreover, significant values of Ni and V were not found in Brazilian fuel oils either. Consideration should be given to the influence of road traffic emissions, emissions from aircraft during take-off and landing, as well as other sources of emissions in the region, such as the Rio de Janeiro military organization of the Brazilian navy (AMRJ). Finally, it has been suggested that random measurements should be made on the funnels of ships at anchor and future plume dispersion studies be conducted.

Author contribution All authors contributed equally to this article.

Data availability The datasets generated and/or analyzed during the current study are available from the corresponding author upon request.

Code availability Not applicable.

Declarations

Conflict of interest The authors declare no competing interests.

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