Impact Assessment of IMO's Sulfur Content Limits: A Case Study at Latin America's Largest Grain Port

Camila Arielle Bufato Moreira[1], Gabriela Polezer[1,2], Jéssica Caroline dos Santos Silva[1], Priscila Caroline de Souza Zorzenão[3], Ana Flavia Locateli Godoi[1], Luciano Fernandes Huergo[4], Carlos Itsuo Yamamoto[3], Yara de Souza Tadano[5], Sanja Potgieter-Vermaa[6,7], Rodrigo Arantes Reis[8], Andrea Oliveira[9], Ricardo Henrique Moreton Godoi[1*]

1- Environmental Engineering Department, Federal University of Paraná, PR, Brazil;
2- Department of Technology, State University of Maringa, PR, Brazil;
3- Chemical Engineering Department, Federal University of Paraná, PR, Brazil;
4- Setor Litoral, Federal University of Paraná, PR, Brazil;
5- Mathematics Department, Federal Technological University of Paraná, PR, Brazil;
6- Ecology & Environment Research Centre, Department of Natural Science, Manchester Metropolitan University, Manchester M1 5GD, United Kingdom;
7- Molecular Science Institute, University of the Witwatersrand, Johannesburg, South Africa;
8- Cell Biology Department, Federal University of Paraná, PR, Brazil;
9- Chemistry Department, Federal University of Paraná, PR, Brazil.

* Corresponding author. E-mail: rhmgodoi@ufpr.br

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Abstract

The world ocean fleet consumes around 4.3 million barrels of heavy fuel oil (HFO) daily, releasing large amounts of sulfur-enriched gaseous and particulate pollutants into the atmosphere. The International Maritime Organization (IMO) has set new sulfur content limit values for HFO under the Global Sulfur Cap 2020 (GSC-2020) program to reduce its environmental and public health impact. This study assesses the environmental benefits of the sulfur content limit values for heavy fuel oil set by the IMO on sulfur emissions, trace element concentrations, and ship related $PM_{2.5}$ pollution at Paranaguá, the largest grain port in Latin America. X-ray Fluorescence analysis revealed that the concentrations of vanadium (V) and nickel (Ni) in $PM_{2.5}$ (i.e., finer particulate matter), which are prevalent trace elements in ship exhaust emissions, decreased significantly from 25.4 ng m^{-3} and 5.8 ng m^{-3} in 2019 to 3.5 ng m^{-3} and 2.2 ng m^{-3} in 2020, respectively. The V/Ni ratio also changed from 4.3 in 2019 to 1.8 in 2020, suggesting significant changes in the signature of marine vessel emission. Sulfur emissions also decreased, with average concentrations of 2.0 µg m^{-3} in 2019 and 1.2 µg m^{-3} in 2020. The primary $PM_{2.5}$ concentration, attributed to ship emissions using V as a tracer, was reduced from ~80% in 2019 (mean = 35.8%) to less than 5% (mean = 4.9%) in 2020. Inhalation exposure to V and Ni in $PM_{2.5}$ showed a decrease in the hazard quotient (HQ) and hazard index (HI) in 2020 compared to 2019, indicating potential health benefits. Our findings underscore the need for more robust international shipping policies prioritizing health objectives and reducing greenhouse gas emissions concurrently. Despite the significant health benefits associated with the implementation of low-sulfur fuels in global shipping, there remains a need for further investigation into the long-term effects of these fuels on air quality and human health.

Keywords: Marine Fuel Oil; Sulfur Limits; Shipping Emissions; Port pollution emissions; Environmental Impact Analysis; $PM_{2.5}$.

Highlights

- GSC-2020 limits sulfur in HFO, reducing environmental and health impacts
- Paranaguá Port air quality shows global emission changes assessed before and after GSC-2020.
- $PM_{2.5}$ sees lower V and Ni in PM2.5, indicating a marine emission shift.
- Lower V, Ni, and sulfur emissions reduce global health risks from maritime pollution.
- GSC-2020 sets new emission standards, impacting policies globally.

1. Introduction

Maritime transport, responsible for 80% of world trade, including approximately 100,000 vessels, generates a staggering 4.3 million barrels of heavy fuel oil (HFO) consumption daily, resulting in significant greenhouse gas emissions and detrimental impacts on human health due to maritime air pollution (IMO, 2020; Slaughter *et al*., 2020; UNCTAD, 2021). Although maritime transport consumes energy efficiently per ton of cargo per kilometer, most ships use marine heavy fuel oil (HFO) as a propellant (Vedachalam *et al*., 2022). HFO generates large quantities of gases and particulate matter (PM) containing elements such as Vanadium (V) and Nickel (Ni), amongst others, into the environment. Black carbon (BC) maritime transport emissions may represent about 2% of global BC emissions (Lack *et al*., 2008).

Around 70% of ship-related exhaust occurs within 400 kilometers of distance from the mainland (Corbett *et al*., 1999; Endresen *et al*., 2003; Eyring *et al*., 2005). As a result, high population density ports and coastal areas may indeed be affected by maritime $PM_{2.5}$ concentrations, which might lead to a rise in mortality rates among workers and the general population (Bencs *et al*., 2020; Corbett *et al*., 1999; ICCT, 2007; Merk, 2014). According to Merk (2014), on average, 230 million people are directly impacted by marine air pollutants in the world's major ports, including NO_2, SO_2, and $PM_{2.5}$. In particular, Winebrake *et al*. (2009) estimated that the $PM_{2.5}$ generated by maritime transport causes an estimated 80,000 premature deaths annually due to cardiovascular and pulmonary diseases. Thus, new mitigation measures are now being explored.

In 2015, the International Maritime Organization (IMO) implemented the so-called Sulfur Emission Control Areas (SECA), reducing HFO sulfur concentration from 1% m/m to 0.1% m/m. Anastasopolos *et al*. (2021), Contini and Merico (2021), Sofiev *et al*. (2018), Spada *et al*. (2018), and Zetterdahl *et al*. (2016) reported on the effects of this regulation. According to Contini and Merico (2021), the GSC 2020 will enable a reduction in maritime emissions of SO_2 and primary PM, thereby facilitating a decrease in the secondary sulfate contained in PM. Reductions in emissions of NO_x, metals, and HPAs contained in PM are also expected. Sofiev *et al*. (2018) predicted that using cleaner fuels could reduce premature mortality and morbidity worldwide by as much as 34% and 54%, respectively. For Latin America and the Caribbean, the authors estimated that the change in fuel could reduce adult and childhood morbidity rates by up to 5% and 12%, respectively. In early 2020, the sulfur content of fuel oils for all ships operating outside the SECA zone was mandated to be decreased from 3.5% m/m to 0.5% m/m (designated as very low sulfur fuel oil – VLSFO). However, studies measuring the benefits of the newly implemented GSC-2020 legislation (DNV, 2020) for the maritime transport community are still in their early stages of development. One of the few studies reported was at a Japanese port surrounded by industrial activities such as power plants and steel mills (Tauchi *et al*., 2022). Tauchi *et al*. (2022) evaluated the changes in SO_2 and NO_x concentrations, as well as the $PM_{2.5}$ elemental compositions of V and Ni (marine fuel tracers), caused by the implementation of the GSC-2020 standard. They found that not only did the SO_2 concentrations (40% reduction) and $PM_{2.5}$ mass concentrations (43% reduction) decrease, but an added benefit was a reduction in V concentrations, leading to a 73% decrease in the V/Ni ratio after the implementation of VLSFO.

We conducted our case study at the port of Paranaguá, the largest grain port in Latin America and the second-largest port in Brazil, which serves as the primary economic hub for the surrounding communities (ANTAQ, 2022; APPA, 2022). The elemental profiles, BC content, and marine fuel tracers were analyzed, and a health risk assessment (hazard quotient (HQ) and the hazard index (HI)) were calculated. This case study provided valuable evidence of the additional environmental and human health benefits that low-sulfur HFO usage in the maritime industry could bring globally. Our methodology could now be used to replicate this analysis in other developing countries and/or the data/evidence being used to leverage policymakers and industry to adhere to the new guideline values. Our case study demonstrated the significant environmental and human health benefits resulting from the implementation of low-sulfur heavy fuel oil (HFO) in the maritime industry. The findings, including the reduction of sulfur emissions, trace elements in ship exhaust emissions, and the improvement in air quality, provide valuable evidence that can be used to influence policymakers and industry practices globally.

2. Materials and Methods

2.1 Site description and $PM_{2.5}$ monitoring

With around 160,000 residents, Paranaguá (25°31'12" S, 48°30'33" W) is in the southern part of Brazil, Figure 1 (IBGE, 2021). The port of Paranaguá is one of the most important routes for the exportation and importation of soybeans, wheat, corn, and fertilizers in Brazil, receiving nearly 2,000 ships and 450,000 trucks that bring a variety of goods to the port on an annual basis (APPA, 2022). The sampling site was strategically chosen within the Port area to represent the surrounding air quality, considering the significant contributions of the port complex, highways and access roads, and diverse industries, particularly fertilizer plants, located in proximity. This ensures that the measurements accurately capture the potential impact of these sources on air pollution levels, as done by Sarmiento *et al*. (2023).

Figure 1. Map of the study area, Port zone of Paranaguá Port, delimited by the green line, represents the area of influence of the port. The sampling site, represented by the blue square, was located 150 meters from the berthing area for ships.

The Paraná Meteorological System (Simepar) and the website database of the National Institute of Meteorology (INMET) were used to obtain the climatological variables that were utilized in this investigation (INMET, 2021; SIMEPAR, 2020). These variables included temperature, relative air humidity, wind speed, and direction, as well as precipitation. Cargo movement reports were provided by the Port Administration of Paranaguá for 2019 and 2020 (APPA, 2022).

A comprehensive weekly $PM_{2.5}$ sampling campaign was conducted from July 02, 2019, to October 31, 2020 (N=60), using low volume Harvard Impactor sampler (Marple *et al*., 1987) with 37 mm polycarbonate filters operated at 10 L min^{-1}. The impactor was positioned at 2.5 m height, free of any obstacles affecting the airflow in the vicinity of the inlet and installed near the main access roads to the port complex and the berthing area for ships (Figure 1). Field blanks (reducing filter handling and transport errors) and samples collected during the campaign were stored at 20 °C ± 5 °C until analysis. To determine $PM_{2.5}$ mass concentration (Method 0500) (NIOSH, 1994), filters were weighed before and after sampling with a microbalance (Sartorius Cubis Micro Balance) and an electrostatic charge eliminator (Sartorius Stat-Pen).

2.2 Chemical analysis

BC determination in $PM_{2.5}$ was carried out using an optical transmissometer (SootScan, OT 21, Magee Scientific Company, Berkeley, USA) with an infrared beam (λ = 880 nm) for a non-destructive analysis of the filters. The attenuation measurements of the transmitted radiation of each filter (in triplicate) and the value of the absorption coefficient of the filter material were considered to determine the BC concentration. The absorption coefficient allows the correction of interference from the absorption of radiation by the filter material.

Quantification of Cr, Cu, Fe, K, Mn, Ni, Pb, V, Zn, Al, S, and Ca were performed in triplicate on 50 % randomly selected samples and blanks, using a Minipal-4 (PANalytical, Almelo, The Netherlands. X-ray Fluorescence analysis (XRF) is a well-established alternative for elemental analysis of aerosol samples. The method has been optimized in our laboratory based on elemental specific reference standards (Micromatter Seattle, WA, USA) and validated by measuring various thin layer standards for each element (Polezer *et al*., 2019). Reference standards were used to obtain calibration curves, verified by measuring multiple thin layer standards for each element and NIST SRM 2783 $PM_{2.5}$ certified reference material (NIST, Gaithersburg, MD) (air particulate on filter media). The limit of detection (LOD) and limit of quantification (LOQ) were calculated as three and ten times, respectively, the inverse of instrumental sensitivity multiplied by the square root of the background noise signal from the analysis of ten blank filters divided by the measurement time. The LOD's (ng m^{-3}) obtained were Cr (0.11), Cu (0.24), Fe (0.18), K (0.53) Mn (0.15), Ni (0.20), Pb (0.25), V (0.06), Zn (0.09), Al (0.41), S (0.30), and Ca (0.18). All results reported in this paper were blank corrected. In this study, data were only pre-processed to exclude outliers resulting from measurement or data entry errors.

2.3 Enrichment factor analysis (EF)

The contribution of anthropogenic sources of PM is often determined using Enrichment Factor analysis, similar to soil analysis, where it is compared to the Earth's crust composition. To that end, a suitable reference element is chosen, which in this case was Si (Alves *et al*., 2015; Hoornaert *et al*., 2004). When EF approaches 1, a source is considered of natural origin. However, values above 10 are classified as enriched with significant contributions from sources other than natural (Liu *et al*., 2003; Godoi *et al*., 2004). The formula for calculating EF is given in Equation 1:

$$EF = \frac{\frac{E_{exp}}{E_{ref}}}{\frac{X_{crust}}{X_{ref\ crust}}} \qquad (1)$$

where X_{exp} is the concentration of an element found in the sample, X_{ref} is the concentration of Si found in the sample, X_{crust} is the concentration of the element defined by nature, and $X_{ref\ crust}$ is the concentration of the Si as determined by Mason (1966).

2.4 Estimation of ship traffic $PM_{2.5}$ emission using V as a tracer

Vanadium (V), the most abundant trace metal in heavy fuel oil (HFO) and a particularly toxic pollutant, can be used as a tracer to calculate the contribution of $PM_{2.5}$ emissions from shipping (Agrawal *et al*., 2009; Corbin *et al*., 2018; Mueller *et al*., 2015) The level of $PM_{2.5}$ in the atmosphere that can be directly ascribed to ship emissions is referred to as "primary $PM_{2.5}$". Equation 2, postulated by Agrawal *et al*. (2009) can be used to derive the primary $PM_{2.5}$ value, which is as follows:

$$PM_{2.5\ (ship)} = \frac{R\ x\ V_a}{FV\ x\ HFO} \qquad (2)$$

where $PM_{2.5(ship)}$ is the primary $PM_{2.5}$ concentration (µg m^{-3}); R is the average ratio of $PM_{2.5}$ to normalized V emitted (8205.8 ppm) according to the HFO burning experiment in vessel engines; V_a is the in situ ambient V concentration (µg m^{-3}); FV.HFO is the average V content (ppm) of HFO used by vessels in port. In this investigation, the value of FV.HFO (65 ± 25 ppm) was an average representative value of samples collected in ports worldwide (Saraga *et al*., 2019; Zhao *et al*., 2013).

2.5 Health risk assessment

Exposure assessment measures contaminant exposure's magnitude, frequency, and duration in a specific population (US EPA, 2011). In addition, health risk assessment estimates the risks associated with exposure to $PM_{2.5}$-bound metals (US EPA, 2009). We assessed the health risk (non-carcinogenic risk) associated with inhalation exposure to selected metals (V and Ni) in the Paranaguá community.

The Inhalation Exposure Concentration (EC) was determined using Equation 3 provided in the Risk Assessment Information System (RAIS, 2022).

$$CE_{(\mu g\ x\ m^{-3})} = \frac{C\ x\ EF\ x\ ED\ x\ ET\ x\ (1day/24\ hours)}{AT\ x\ ED} \tag{3}$$

where C (μg m^{-3}) is the trace element concentration measured in this study. EF (350 days $year^{-1}$) is the exposure frequency. ED (26 years) is the exposure duration for adults. ET (24 hours a day^{-1}) is the daily exposure time. AT (365 days $year^{-1}$) is the average lifetime.

In addition, we measured Hazard Quotient (HQ) (Equation 4); the quotient describes the non-carcinogenic risk of each pollutant that enters the human body through the respiratory route.

$$HQ = \frac{EC}{Toxicity\ value\ x\ 1000} \tag{4}$$

where HQ (unitless) is the Hazard Quotient, EC ($\mu g \cdot m^{-3}$) is the exposure concentration, and Toxicity value (mg m^{-3}) = Inhalation toxicity value (e.g., RfC or RfD). The RfD values used in this study were Ni = 1.4×10^{-5} and V= 1.0×10^{-4} (Lovett *et al.*, 2018; OEHHA, 2012; US EPA, 2015; Zhang *et al.*, 2021). The HQ of V and Ni was calculated and then summed to obtain the risk index (HI) (US EPA, 2011, 2009).

The nonparametric Mann-Whitney U test emerged as a valuable statistical tool for assessing differences in median values of the time series of air pollutant concentrations in this study. This method proved effective in addressing challenges related to non-normal data distributions, enabling the identification of statistically significant differences among exposure groups.

The insights gained from these findings are crucial for comprehending the potential health consequences of air pollution. The R programming language (R Core Team, 2019) was employed for statistical analysis, and the nonparametric Mann-Whitney test was executed to determine significance. In addition, pollution Rose graphical representations were plotted using the OpenAir package in R (Carslaw and Ropkins, 2012), as a complement to understand the effect of wind direction on the dispersion of $PM_{2.5}$.

In line with the rigorous standards of scientific inquiry, it is imperative to acknowledge potential sources of uncertainty, including sampling variability, potential biases, and limitations associated with the chosen analytical techniques. This acknowledgment enhances the transparency and reliability of our study's findings and conclusions.

3. Results and Discussion

Our study reveals a significant decrease in pollutant concentrations, an altered V/Ni ratio, reduced sulfur emissions, lowered primary $PM_{2.5}$ concentration, and an improved health risk following the implementation of GSC-2020.

3.1 Ambient concentrations of $PM_{2.5}$ and meteorological parameters

To understand the air quality dynamic due to interactions between long-range and local transport of pollutants, meteorological parameters, including daily precipitation and temperature for 2019 and 2020, were meticulously compared with historical data spanning from 1972 to 2018, as illustrated in Figure S1. Analysis of data from Figures S2 and S3, along with Table S1, reveals that the average wind speed in both 2019 and 2020 was measured to be 2 m/s. This consistent wind speed across both years suggests a relatively stable wind climate in the study area.

To comprehend the dynamics of air quality influenced by interactions among pollutant emissions, the indirect impacts of precipitation gradients on $PM_{2.5}$ concentration were examined across different seasons. For that purpose, the $PM_{2.5}$ mass concentration data (from 2019 to 2020) were compared against rainfall conditions (Fig. 2). It ranged from 4.7 to 15.2 µg m^{-3} (mean 9.2 ± 2.9 µg m^{-3}). The mean mass concentration of $PM_{2.5}$ has been measured to exceed the newly recommended annual mean concentration of 5 µg m^{-3} established by the World Health Organization (WHO) guidelines in 2021.

Figure 2. The $PM_{2.5}$ and BC concentrations in Paranaguá over the sampling period (weekly) from the first week of July 2019 to the second week of October 2020.The black dashed line represents precipitation (mm).

$PM_{2.5}$ concentrations at the port of Paranaguá were comparable to those observed in Venice (9.4 µg m^{-3}), despite Venice hosting nearly twice the number of docked ships (Contini *et al*., 2011). The port of Venice is subjected to significant influences from the heavy traffic of goods and cruise ships as well as by industrial activities, including metallurgical and oil industries and coal power plants (Contini *et al*., 2015; Gregoris *et al*., 2021; Masiol *et al*., 2010). Healy *et al*. (2010) also reported $PM_{2.5}$ concentrations at the port of Cork in Ireland as those observed in Venice (9.7 µg m^{-3}). Similar to Paranaguá Port, Cork Port accommodates a comparable number of vessels and is situated adjacent to Ireland's largest electricity generation facility and an oil refinery (Healy *et al*., 2010; Hellebust *et al*., 2010). Although the comparative studies have different timeframes, the fact of similar concentrations of $PM_{2.5}$ is interesting. Common sources of emissions, such as ship traffic, exist among the three ports mentioned; however, the industrial complexes' activities differ. This disparity suggests that chemically, $PM_{2.5}$ characteristics with equivalent mass concentrations may induce variable effects on human health, as indicated by Park *et al*. (2018). The GSC-2020 reduction program faced a unique challenge due to its timing. The COVID-19 pandemic, with its sudden decrease in port shipping activity, complicated the comparison of $PM_{2.5}$ concentrations pre- and post- the program's implementation. For example, Tauchi *et al*. (2022) reported that $PM_{2.5}$ concentration in the Seto Inland Sea, a semi-enclosed sea with international shipping port terminals, decreased by up to 43% between 2018 and 2020. This reduction may be associated with the stagnation of economic activities due to the COVID-19 pandemic and decreased transport of $PM_{2.5}$ after emission control measures were implemented in Japan.

On the other hand, export and import activities were not significantly affected by the COVID-19 pandemic. The evaluation was made according to the cargo movement reports, monthly data on the volume of trucks moving through the port of Paranaguá, and the polar plot tool, which groups wind speed and direction with pollutant concentration (Figure S5, Figure S6). The Paranaguá Port, in 2020, received more than 45,000 heavy vehicles per month, a 10% increase compared to the previous year (APPA, 2022). This increase in traffic may have contributed to the port's $PM_{2.5}$ level (9.3 ± 2.4 µg m^{-3}) in 2020. The polar plot tool revealed that the $PM_{2.5}$ concentration peaks were modified (Figure S6). The contributions for 2019 and 2020 are in different directions and may indicate different emissions sources, predominantly road transport for 2020. In 2019, the main contributions came from the vessel maneuvering and docking region.

3.2 Black Carbon Levels (BC)

The BC concentrations in $PM_{2.5}$ were measured to estimate BC emissions from combustion engines on land and at sea. Figure 2 displays that the mean concentration for the entire sampling period was 1.4 ± 0.3 µg m^{-3}, with concentrations ranging from 0.98 to 2.4 µg m^{-3}. BC percentages in $PM_{2.5}$ were constant and made up around 16% of the total mass of $PM_{2.5}$ on average. Considering that the Port is operational 24 hours/day, the activities of displacement and transport of loads, as well as the movement of trucks and vehicles in the urban area of Paranaguá, may be responsible for the BC contribution percentages without significant variations over the study period.

The BC values found in Paranaguá are comparable to those found by Gobbi *et al.* (2020) (1.3 µg m^{-3}) in the port of Civitavecchia, Italy, which has significant cruise ships and cargo ship traffic, totaling about 3,000 ships per year, which is approximately 1,000 more vessels than port of Paranaguá. The BC concentration at the port of Paranaguá did not show any significant change ($p>0.05$) from 2019 to 2020 (1.44 and 1.45 µg m^{-3}, respectively) (Figure S4). This finding aligns with emissions simulations modeled by Ji and El-Halwagi (2020), which demonstrated the limited effectiveness of GSC-2020 in controlling or reducing BC emissions.

Analyzing the spatial distribution of BC concentrations by the polar plot tool, we observed that BC's dispersion showed minor differences between 2019 and 2020. The south direction was intensified in 2020, characterizing truck access roads to the port complex. However, higher concentrations were most prevalent in both years in the northeastern, southeast, and eastern directions. These directions correspond to the region where vessels access, maneuver, dock, and cargo handling (Figure S6). The contribution of BC to Paranaguá port can also be attributed to other local emission sources, such as the trucks that transport goods to the port. Higher volume of vehicular traffic is recurrently related with higher $PM_{2.5}$-BC content (Ambade *et al.*, 2022), mostly was associated with heavy-duty diesel emission (Andrade *et al.*, 2012). Road transport is one of Brazil's primary logistics systems, moving approximately 60% of the country's goods (Bottasso *et al.*, 2021). The harvesting of grains is an example of a time when there was a significant increase in cargo volume moving through the port of Paranaguá, which resulted in an expressive movement of 40,000 trucks in a season.

3.3 Elemental profiles and Enrichment factor analysis (EF)

The EF was used to determine whether the elemental concentration of the aerosol originates from natural or anthropogenic sources. The elemental profiles, as measured by XRF analysis, are presented in Table S2. Reductions in the elemental concentrations of Ca, Ni, V, and S were observed during the 2020 campaign, while the concentrations of Zn, Pb, Cu, Cr, and Mn increased compared to the previous year. The EF results, Figure 3, suggest that the crustal-related elements K, Fe, Ca, and Al (EF close to 1) could be attributed to the resuspension of soil (Agarwal *et al.*, 2011; Andrade *et al.*, 2012; Dwivedi *et al.*, 2006; Viana *et al.*, 2008; Wang *et al.*, 2003). The other chemical elements, S>Pb>Zn>Ni>V>Cu, were enriched above the crustal reference (i.e., EF>10), indicating that they were probably produced by anthropogenic activities (Zhang *et al.*, 2021).

The only elements that showed significant EF value variances between 2019 and 2020 were S, V, and Ni, indicating that $PM_{2.5}$ was significantly more enriched with these elements in 2019 compared to 2020. These three elements are tracers for combustion processes, especially HFO (Moldanová *et al*. 2009). The EF-S reduced by 2020, which could be due to the S-bound $PM_{2.5}$ concentrations decreasing by 40% ($p < 0.05$) between 2019 (2.0 μg m^{-3}) and 2020 (1.2 μg m^{-3}), as can be seen in Figure S4. Similarly, the EF-Ni and EF-V values decreased and could be ascribed to the significant elemental concentration reduction ($p<0.05$) of V and Ni of 86% and 62%, respectively, from 2019 (25.4 ng m^{-3} V and 5.8 ng m^{-3} Ni) to 2020 (3.5 ng m^{-3} V and 2.2 ng m^{-3} Ni).

Marine fuels with high concentrations of sulfur are more enriched with heavy metals, such as V and Ni (Agrawal *et al*., 2008; Anastasopolos *et al*., 2021). Anastasopolos *et al*. (2021) and Spada *et al*. (2018) also reported such reductions after the implementation of low-sulfur marine fuel regulation in Sulfur Emission Control Areas (SECA). While other factors may contribute, the data suggests that the 2020 implementation of VLSFO likely played a significant role in reducing S-bound $PM_{2.5}$, nickel, and vanadium.

Figure 3. Enrichment factors for 2019 and 2020. Boxplots show the median, 25th, and 75th percentile. The line EF = 10 indicates that the elements above the line are enriched when compared to the reference element.

While the role of VLSFO in reducing S-bound $PM_{2.5}$, nickel, and vanadium is evident, other sources dominate for heavy metals like zinc, lead, copper, chromium, and manganese. Their concentrations are primarily associated with heavy vehicular emissions, brake contact, tire wear, and lubrication oil, as documented in previous studies (Amato *et al*., 2011; Brito *et al*., 2013; Andrade *et al*., 2012). The increased number of trucks in 2020, particularly during grain harvest periods, likely contributed to the observed rise in these elements' concentrations in $PM_{2.5}$.

3.4 V/Ni ratio present in $PM_{2.5}$

Vanadium (V) and nickel (Ni) are the most abundant trace metals in ship exhaust particulate matter (Corbin *et al*., 2018), and the V/Ni ratio acts as a HFO combustion tracer/marker (Agrawal *et al*., 2009; Corbin *et al*., 2018; Mueller *et al*., 2015). Since both V and Ni could have other sources (industrial emissions, power plants, oil refineries) and literature values estimate typical V/Ni ratio of emissions from marine vessels to be between 2.5 and 5 (Cesari *et al*., 2014; Gregoris *et al*., 2016; Pandolfi *et al*., 2011; Saraga *et al*., 2019; Viana *et al*., 2009; Zhao *et al*., 2013), it could be expected that the V/Ni ratio will change during the two years investigated.

In this study, the V/Ni ratio in $PM_{2.5}$ for the years 2019 and 2020 resulted in 4.3 ± 0.8 (within the typical range) and 1.8 ± 0.6 (outside the typical range), respectively (Table S3 and Figure 4). In 2019, the ratio was higher than those found by Saraga *et al*. (2019) (2.7) at the port of Thessaloniki, Greece, and by Bove *et al*. (2014) (2.8) in the port region of Genoa, Italy. Conversely, the 2019's ratio (4.3 ± 0.8) fell within the range observed at the port of Melilla, Spain (4.0) (Viana *et al*., 2009). This finding offers a contrasting perspective to the deviations seen in Thessaloniki and Genoa ports, suggesting potential regional factors influencing the V/Ni ratio of $PM_{2.5}$.

A substantial shift in the V/Ni ratio observed in $PM_{2.5}$ composition (Figure 4) suggests a notable change in the contribution of marine vessel emissions in 2020. This shift is likely driven by the differential reductions in V and Ni concentrations, with V exhibiting a significantly steeper decline compared to Ni (Section 3.3). This observed pattern aligns with the implementation of the GSC-2020 regulation, which aimed to reduce sulfur content and heavy metal emissions from marine fuels. Similar findings have been reported elsewhere; Tauchi *et al*. (2022) observed a comparable decrease in the V/Ni ratio in Japan, with values falling from a range of 1.6-4.0 in 2019 to 0.6-1.1 in 2020. These findings provide evidence of a significant reduction in the contribution of these metals in marine vessel emissions to $PM_{2.5}$ in 2020.

Figure 4. Time series of V and Ni concentrations along the sampling period (weekly) from the 1st week of July 2019 to the 2nd week of October 2020 in Paranaguá. The brown dashed line indicates V/Ni ratio.

3.5 Primary $PM_{2.5}$ Contribution

To quantify the contribution of shipping emissions to primary $PM_{2.5}$ at Paranaguá Port, we adopted the tracer-based approach utilized by Agrawal *et al*. (2009). This method leverages vanadium (V) as a marker for ship engine combustion, capitalizing on its well-established link to emissions from this source (Agrawal *et al*., 2009; Saraga *et al*., 2019; Viana *et al*., 2014; Zhao *et al*., 2013).

As shown in Figure 5, the primary $PM_{2.5}$ fraction of total $PM_{2.5}$ mass peaked in 2019, reaching a maximum contribution of approximately 80%. This striking observation suggests that ship emissions and associated port activities were the dominant contributors to fine particulate matter at Paranaguá Port during that year. The V tracer method may present a limitation concerning underestimating the primary contribution of shipping to $PM_{2.5}$ in fuels with lower sulfur content, such as VLSFO. Nonetheless, due to the absence of an alternative method, the constants established by Agrawal *et al*., 2009, were retained. It is recommended to optimize the method for future research, considering the current imperative of utilizing cleaner new fuels.

Figure 5. Time series of primary $PM_{2.5}$ contributions along the sampling period from the 1st week of July 2019 to the 2nd week of October 2020 in Paranaguá. The black line indicates the percentage of the primary $PM_{2.5}$ contribution to the total $PM_{2.5}$ (%).

Figure 5 demonstrates a significant reduction in primary $PM_{2.5}$ attributed to ship emissions in 2020. Vanadium (V) concentrations, a well-established tracer for ship engine combustion, exhibited a statistically significant decrease ($p < 0.05$) compared to 2019.

This decline is further reflected in the average percentage contribution of primary $PM_{2.5}$ to total $PM_{2.5}$, which plummeted from 36% in 2019 to 5% in 2020 (Table 1). While the COVID-19 pandemic undoubtedly impacted global shipping patterns, the port of Paranaguá remained largely unaffected, with cargo traffic increasing in 2020 (Table S4). This suggests that the observed decrease in primary $PM_{2.5}$ contributions from moored ships is likely attributable to factors other than pandemic restrictions, such as potential changes in fuel types, emission regulations, or ship operations.

Table 1 highlights the significantly higher primary $PM_{2.5}$ concentrations and ship emission contributions observed in this study compared to earlier works by Agrawal *et al*. (2009), Cesari *et al*. (2014), Saraga *et al*. (2019), and Zhao *et al*. (2013). This disparity could be attributed to various factors, including a) Variations in ship engine technology and operational practices; b) Specific characteristics of the port and surrounding environment.

Table 1. Comparison of primary $PM_{2.5}$ concentration and percentage contribution of ship emissions to total $PM_{2.5}$ by different studies in port-cities.

The significant differences in local activities across the compared ports warrant consideration when interpreting their $PM_{2.5}$ emissions. Yangshan, part of the Shanghai port complex, ranks among the world's busiest container hubs (Zhao *et al*., 2013). In contrast, Brindisi in Italy sits adjacent to a central industrial zone and experiences a diverse ship population, including coal carriers, bulk cargo ships, and tourist vessels

(Cesari *et al.*, 2014). With its metropolitan population exceeding one million, Thessaloniki is the second-largest Greek seaport and a prominent player in the East Mediterranean basin (Saraga *et al.*, 2019).

Paranaguá, on the other hand, is uniquely situated near one of the most significant remnants of Brazil's Atlantic Forest Reserve (UNESCO, 1999). Port operations, primarily focused on grain exports, and related agricultural industries, such as fertilizer processing and storage, dominate the local economy. Consequently, ship emissions constitute the major contributor to $PM_{2.5}$ in Paranaguá. These findings highlight the significant impact of traffic and ship berthing on air quality within Paranaguá Port, particularly in 2019.

3.6 Health risk assessment

Assessing the risks to human health posed by the concentration of $PM_{2.5}$ produced by ships is essential. It is possible that the heavy metals present in $PM_{2.5}$, despite being present in low concentrations, could cause damage to both human health and the environment due to their high toxicity levels (Mamoudou *et al.*, 2018). Measuring the potential toxicity of particles and their short- and long-term effects on health can prevent future public health impacts (Park *et al.*, 2018).

This study evaluated the health risks of non-carcinogenic effects caused by the elemental concentrations of V and Ni in ship emissions. The Exposure Concentration (EC) of both vanadium (V) and nickel (Ni) decreased significantly in 2020 compared to 2019 (Table 2). Vanadium EC dropped from 2.4×10^{-2} µg m^{-3} to 3.5×10^{-3} µg m^{-3}, while Ni EC fell from 5.5×10^{-3} µg m^{-3} to 2.1×10^{-3} µg m^{-3}. As EC directly relates to the potential toxicity of inhaled particles, these reductions suggest a potentially lower risk of adverse health effects associated with V and Ni exposure from this source. This observed trend aligns with the previously reported decreases in elemental V and Ni concentrations, further strengthening the evidence for improved air quality.

Using a hazard-based method, the Hazard Quotient (HQ) and the Hazard Index (HI) of each element (V and Ni) were calculated for adults (US EPA). Table 2 shows the findings from the HQ and HI to estimate the non-carcinogenic effects of trace elements in $PM_{2.5}$. HQ or HI above 1 indicates probable adverse effects (Liu *et al.*, 2015; Lovett *et al.*, 2018; RAIS, 2022; US EPA, 2009; Zhu *et al.*, 2021). In 2019 and 2020, the average HQ values for V were 0.24 and 0.04, respectively. Ni also decreased, with average HQ values of 0.40 (in 2019) and 0.15 (in 2020). The resulting HI for the entire study period decreased from 0.64 (2019) to 0.18 (2020) (Table 2) concerning V and Ni concentrations and exposures.

Table 2. Hazard Quotient (HQ), Inhalation Exposure Concentration (EC) and Hazard Index (HI) for vanadium and nickel along the sampling period between 2019 and 2020

Throughout the study period, neither the Hazard Quotient (HQ) nor the Hazard Index (HI) exceeded 1 for V and Ni in $PM_{2.5}$. However, the significant reduction in HI for 2020 (72%) compared to 2019 suggests a notable decrease in exposure to potential non-carcinogenic effects, particularly from these metals. This aligns with the established understanding that improved air quality reduces health risks, as confirmed by previous studies (Ding *et al.*, 2019; Kumar *et al.*, 2020; Li *et al.*, 2021; Rojas-Lemus *et al.*, 2021; Shi *et al.*, 2022; Zhao *et al.*, 2022; Liu *et al* 2023; Shetaya *et al.*, 2023).

3.7. Future consideration and implications

Enhancing Study Comprehensiveness: Our research acknowledges the necessity of a broader assessment. To this end, we advocate for future studies to expand the sample size by incorporating more ports and vessels. Such an expansion would yield a more holistic understanding of the environmental advantages of the Global Sulfur Cap 2020 (GSC-2020) initiative, extending the insights gained from this case study to a broader context.

Economic and Technological Challenges: Mitigating sulfur emissions in maritime shipping presents economic and technological hurdles. The adoption of low-sulfur fuels is influenced by many factors, including their availability, cost, emission reduction technologies, engine conversion expenses, and environmental regulations. Shipping companies must navigate these complexities, weighing the costs against the benefits amidst evolving market conditions and regulatory landscapes.

Alternative Fuel Sources: Our study highlights the imperative for further investigation into the efficacy of alternative fuel sources, such as liquefied natural gas (LNG) or battery-powered vessels, in curbing air pollution and greenhouse gas emissions from maritime transport.

Compliance Measurement and Challenges: Various methods like fuel oil sampling, ship document checks, and sulfur emission monitoring are proposed to verify GSC-2020 compliance. Challenges, including fuel accessibility, cost, fuel blend stability, and emission tech efficiency, are outlined. Policy interventions like operator training, fuel quality standards, emission reduction best practices, and improved monitoring and enforcement are advised to tackle these.

Co-benefits of GSC-2020: While the ancillary benefits of the GSC-2020 program on environmental and public health still need to be explored, they hold significant promise. Citing the International Maritime Organization (IMO), the study notes that the program could avert approximately 570,000 premature deaths and 14 million cases of childhood asthma globally between 2020 and 2025. Additionally, it could enhance air quality in coastal regions, particularly in continents like Asia, Africa, and Latin America, which are major hubs of maritime traffic.

Social and Equity Impacts: While our research did not specifically assess the social and equity impacts of the GSC-2020 program, examining these issues is stressed. These impacts are particularly relevant to low-income communities and developing countries dependent on maritime trade. Developing comprehensive strategies to address the heightened costs and competitive imbalances in the global shipping sector is crucial.

Technological Advancements and Opportunities: The GSC-2020 program opens avenues for groundbreaking innovations in maritime technology. These advancements could lead to improved engine designs for better fuel efficiency and emission reduction, the creation of additives to neutralize pollutants in traditional fuels, the exploration of alternative propulsion systems, the research into sustainable e-fuels, and the adoption of operational practices like route optimization and 'slow steaming' to further reduce emissions.

Interdisciplinary Research and Collaboration: The critical role of interdisciplinary research and collaboration among various scientific fields, stakeholder groups, and policy frameworks is vital. Such concerted efforts are deemed essential to effectively address the complex environmental challenges posed by global shipping and foster sustainable practices within the industry.

Long-term effects of the GSC-2020 program: The long-term investigation can assess the sulfur cap's effectiveness in reducing pollution and identify changes in pollutant composition near ports and in wider regions affected by maritime transport. The reduced sulfur emissions may impact coastal environments. Hence, monitoring water quality, ecosystem dynamics, and marine organism abundance is crucial to understanding the program's ecological effects and identifying potential trade-offs.

Potential impacts of the GSC-2020 on marine ecosystems: While reducing sulfur emissions from ships benefits air quality, it may indirectly affect marine biogeochemistry. Released sulfur compounds contribute to acid rain and nutrient deposition, potentially altering nutrient availability and disrupting ecosystems. The program's success hinges on understanding these potential trade-offs. Further research focusing on changes in nutrient cycling, primary production, and species distribution in response to reduced sulfur and PM emissions is crucial for a holistic assessment of the program's ecological impact.

Interactions between air pollution and climate change impact on marine ecosystems and human health: By integrating data on air pollution, climate change, marine ecosystems, and human health, researchers can better understand the interactions and potential synergistic effects between these factors. This knowledge could contribute to developing effective mitigation and adaptation strategies to protect marine ecosystems and human populations from the combined impacts of air pollution and climate change.

Potential role of international cooperation and governance: This study highlights the importance of international cooperation and governance, such as the regulations set by the IMO. These frameworks are critical in establishing emission standards and promoting sustainable practices within the maritime industry. The study's focus on sulfur content limits and their impact underscores the necessity of coordinated efforts and common standards for tackling air pollution and climate change challenges in global shipping. While the research does not explore the specific mechanisms of international cooperation, it does provide valuable evidence for the environmental benefits of implementing such measures.

The potential role of stakeholder: The International Maritime Organization administration could explore the potential role of stakeholder engagement and participation in shaping policy decisions related to global shipping and environmental sustainability. This could involve local communities, NGOs, or industry representatives in decision-making processes. By incorporating diverse perspectives and expertise from stakeholders, the IMO can develop more inclusive and effective policies that address the complex challenges of sulfur emissions and environmental sustainability in the maritime industry. This approach can enhance transparency, accountability, and legitimacy in policymaking while fostering collaborative efforts toward achieving shared environmental protection and sustainable development goals.

4. Conclusion

Evaluating the effectiveness of legal instruments like the Global Sulfur Cap 2020 in improving air quality is critical, as it provides quantitative evidence of their environmental impact. This study investigated the Port of Paranaguá as a case study to assess the influence of port activities on $PM_{2.5}$ emissions and trace element composition. Between 2019 and 2020, we observed a statistically significant ($p < 0.05$) decrease in the V/Ni ratio, indicating a reduced contribution of ship emissions to $PM_{2.5}$. Notably, primary $PM_{2.5}$ concentration from ship emissions declined by over 8% in 2020, leading to a concomitant reduction in inhalation exposure and both Hazard Quotient (HQ) and Hazard Index (HI) values. These findings suggest a reduction in exposure to the potential non-cancer effects of $PM_{2.5}$, especially toxic elements.

Our work presents evidence demonstrating the favorable influence of the Global Sulfur Cap 2020 on air quality, providing essential insights for the global air pollution community. This finding holds significance due to the considerable role that shipping plays in global $PM_{2.5}$ emissions. Improvements in air quality have already been observed in certain port cities and coastal regions. Consequently, populations living near these areas may experience decreased respiratory illnesses and other positive health outcomes. However, further research is necessary to quantify the long-term health and environmental benefits of the Sulfur Cap, particularly regarding chronic exposure effects from reduced pollution levels. Furthermore, continued efforts like developing new technologies like hybrid and electric ships and using alternative fuels like liquefied natural gas could amplify these positive trends and safeguard air quality for all.

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REFERENCES

Agarwal, D., Singh, S.K., Agarwal, A.K., 2011. Effect of Exhaust Gas Recirculation (EGR) on performance, emissions, deposits and durability of a constant speed compression ignition engine. Appl Energy 88, 2900–2907. https://doi.org/10.1016/j.apenergy.2011.01.066.

Agrawal, H., Eden, R., Zhang, X., Fine, P.M., Katzenstein, A., Miller, J.W., Ospital, J., Teffera, S., Cocker, D.R., 2009. Primary particulate matter from ocean-going engines in the Southern California Air Basin. Environ Sci Technol 43, 5398–5402. https://doi.org/10.1021/es8035016.

Agrawal, H., Welch, W.A., Miller, J.W., Cocker, D.R., 2008. Emission measurements from a crude oil tanker at sea. Environ Sci Technol 42, 7098–7103. https://doi.org/10.1021/es703102y.

Alves, C.A., Gomes, J., Nunes, T., Duarte, M., Calvo, A., Custódio, D., Pio, C., Karanasiou, A., Querol, X., 2015. Size-segregated particulate matter and gaseous emissions from motor vehicles in a road tunnel. Atmos Res 153, 134–144. https://doi.org/10.1016/j.atmosres.2014.08.002.

Amato, F., Pandolfi, M., Moreno, T., Furger, M., Pey, J., Alastuey, A., Bukowiecki, N., Prevot, A.S.H., Baltensperger, U., Querol, X., 2011. Sources and variability of inhalable road dust particles in three European cities. Atmos Environ 45, 6777–6787. https://doi.org/10.1016/j.atmosenv.2011.06.003.

Anastasopolos, A.T., Sofowote, U.M., Hopke, P.K., Rouleau, M., Shin, T., Dheri, A., Peng, H., Kulka, R., Gibson, M.D., Farah, P.M., Sundar, N., 2021. Air quality in Canadian port cities after regulation of low-sulphur marine fuel in the North American Emissions Control Area. Science of The Total Environment 791, 147949. https://doi.org/10.1016/j.scitotenv.2021.147949.

Ambade, B., Sankar, T. K., Sahu, L. K., Dumka, U. C., 2022. Understanding Sources and Composition of Black Carbon and PM2.5 in Urban Environments in East India. Urban Science 6 (3), 60. https://doi.org/10.3390/urbansci6030060.

Andrade, M. F., de Miranda, R.M., Fornaro, A., Kerr, A., Oyama, B., de Andre, P.A., Saldiva, P., 2012. Vehicle emissions and PM 2.5 mass concentrations in six Brazilian cities. Air Qual Atmos Health 5, 79–88. https://doi.org/10.1007/s11869-010-0104-5.

ANTAQ, 2022. Setor portuário movimenta 1,2 bilhão de toneladas de cargas em 2021 [WWW Document]. Agência Nacional de Transportes Aquaviários (ANTAQ). URL https://www.gov.br/antaq/pt-br/noticias/2022/setor-portuario-movimenta-1-2-bilhao-de-toneladas-de-cargas-em-2021 (accessed 12.12.23).

APPA, 2022. Dados Gerais | Administração dos Portos de Paranaguá e Antonina [WWW Document]. Administração dos Portos de Paranaguá e Antonina. URL https://www.portosdoparana.pr.gov.br/Operacional/Pagina/Dados-Gerais (accessed 12.12.23).

Bencs, L., Horemans, B., Buczyńska, A.J., Deutsch, F., Degraeuwe, B., Van Poppel, M., Van Grieken, R., 2020. Seasonality of ship emission related atmospheric pollution over coastal and open waters of the North Sea. Atmos Environ X 7, 100077. https://doi.org/10.1016/J.AEAOA.2020.100077.

Bottasso, A., Conti, M., Costacurta de Sa Porto, P., Ferrari, C., Tei, A., 2021. Roads to growth: The Brazilian way. Research in Transportation Economics 90, 101086. https://doi.org/10.1016/J.RETREC.2021.101086.

Bove, M.C., Brotto, P., Cassola, F., Cuccia, E., Massabò, D., Mazzino, A., Piazzalunga, A., Prati, P., 2014. An integrated PM2.5 source apportionment study: Positive Matrix Factorisation vs. the chemical transport model CAMx. Atmos Environ 94, 274–286. https://doi.org/10.1016/j.atmosenv.2014.05.039.

Brito, J., Rizzo, L. V., Herckes, P., Vasconcellos, P.C., Caumo, S.E.S., Fornaro, A., Ynoue, R.Y., Artaxo, P., Andrade, M.F., 2013. Physical–chemical characterisation of the particulate matter inside two road tunnels in the São Paulo Metropolitan Area. Atmos Chem Phys 13, 12199–12213. https://doi.org/10.5194/acp-13-12199-2013.

Carslaw, D.C., Ropkins, K., 2012. openair — An R package for air quality data analysis. Environmental Modelling & Software 27–28, 52–61. https://doi.org/10.1016/j.envsoft.2011.09.008.

Cesari, D., Genga, A., Ielpo, P., Siciliano, M., Mascolo, G., Grasso, F.M., Contini, D., 2014. Source apportionment of PM2.5 in the harbour–industrial area of Brindisi (Italy): Identification and estimation of the contribution of in-port ship emissions.

Science of The Total Environment 497–498, 392–400. https://doi.org/10.1016/j.scitotenv.2014.08.007.

Contini, D., Gambaro, A., Belosi, F., De Pieri, S., Cairns, W.R.L., Donateo, A., Zanotto, E., Citron, M., 2011. The direct influence of ship traffic on atmospheric PM2.5, PM10 and PAH in Venice. J Environ Manage 92, 2119–2129. https://doi.org/10.1016/j.jenvman.2011.01.016.

Contini, D., Gambaro, A., Donateo, A., Cescon, P., Cesari, D., Merico, E., Belosi, F., Citron, M., 2015. Inter-annual trend of the primary contribution of ship emissions to PM2.5 concentrations in Venice (Italy): Efficiency of emissions mitigation strategies. Atmos Environ 102, 183–190. https://doi.org/10.1016/j.atmosenv.2014.11.065.

Contini, D., Merico, E., 2021. Recent Advances in Studying Air Quality and Health Effects of Shipping Emissions. Atmosphere 12, 92. https://doi.org/10.103390/atmos1210092.

Corbett, J.J., Fischbeck, P.S., Pandis, S.N., 1999. Global nitrogen and sulfur inventories for oceangoing ships. Journal of Geophysical Research: Atmospheres 104, 3457–3470. https://doi.org/10.1029/1998JD100040.

Corbin, J.C., Mensah, A.A., Pieber, S.M., Orasche, J., Michalke, B., Zanatta, M., Czech, H., Massabò, D., Buatier De Mongeot, F., Mennucci, C., El Haddad, I., Kumar, N.K., Stengel, B., Huang, Y., Zimmermann, R., Prévôt, A.S.H., Gysel, M., 2018. Trace Metals in Soot and PM2.5 from Heavy-Fuel-Oil Combustion in a Marine Engine. Environ Sci Technol 52, 6714–6722. https://doi.org/10.1021/acs.est.8b01764.

Ding, D., Xing, J., Wang, S., Liu, K., Hao, J., 2019. Estimated contributions of emissions controls, meteorological factors, population growth, and changes in baseline mortality to reductions in ambient pm2:5 and pm2:5-related mortality in china, 2013–2017. Environ Health Perspect 127. https://doi.org/10.1289/EHP4157.

DNV, 2020. Global Sulphur Cap 2020 - DNV [WWW Document]. Det Norske Veritas group. URL https://www.dnv.com/maritime/global-sulphur-cap/index.html (accessed 12.13.21).

Dwivedi, D., Agarwal, A.K., Sharma, M., 2006. Particulate emission characterization of a biodiesel vs diesel-fuelled compression ignition transport engine: A comparative study. Atmos Environ 40, 5586–5595. https://doi.org/10.1016/j.atmosenv.2006.05.005.

Endresen, Ø., Sørgård, E., Sundet, J.K., Dalsøren, S.B., Isaksen, I.S.A., Berglen, T.F., Gravir, G., 2003. Emission from international sea transportation and environmental impact. Journal of Geophysical Research: Atmospheres 108, 4560. https://doi.org/10.1029/2002JD002898.

Eyring, V., Köhler, H.W., Van Aardenne, J., Lauer, A., 2005. Emissions from international shipping: 1. The last 50 years. Journal of Geophysical Research: Atmospheres 110, 171–182. https://doi.org/10.1029/2004JD005619.

Gobbi, G.P., Di Liberto, L., Barnaba, F., 2020. Impact of port emissions on EU-regulated and non-regulated air quality indicators: The case of Civitavecchia (Italy). Science of The Total Environment 719, 134984. https://doi.org/10.1016/j.scitotenv.2019.134984.

Godoi, R.H.M., Godoi, A.F.L., Worobiec, A., Andrade, S.J., de Hoog, J., Santiago-Silva, M.R., Van Grieken, R. 2004. Characterisation of sugar cane combustion particles in the Araraquara region, Southeast Brazil. Microchimica Acta 145, 53-56. https://doi.org/10.1007/s00604-003-0126-x.

Gregoris, E., Barbaro, E., Morabito, E., Toscano, G., Donateo, A., Cesari, D., Contini, D., Gambaro, A., 2016. Impact of maritime traffic on polycyclic aromatic hydrocarbons, metals and particulate matter in Venice air. Environmental Science and Pollution Research 23, 6951–6959. https://doi.org/10.1007/S11356-015-5811-x.

Gregoris, E., Morabito, E., Barbaro, E., Feltracco, M., Toscano, G., Merico, E., Grasso, F.M., Cesari, D., Conte, M., Contini, D., Gambaro, A., 2021. Chemical characterization and source apportionment of size-segregated aerosol in the port-city of Venice (Italy). Atmos Pollut Res 12, 261–271. https://doi.org/10.1016/j.apr.2020.11.007.

Healy, R.M., Hellebust, S., Kourtchev, I., Allanic, A., O'Connor, I.P., Bell, J.M., Healy, D.A., Sodeau, J.R., Wenger, J.C., 2010. Source apportionment of PM2.5 in Cork Harbour, Ireland using a combination of single particle mass spectrometry and quantitative semi-continuous measurements. Atmos Chem Phys 10, 9593–9613. https://doi.org/10.5194/acp-10-9593-2010.

Hellebust, S., Allanic, A., O'Connor, I.P., Jourdan, C., Healy, D., Sodeau, J.R., 2010. Sources of ambient concentrations and chemical composition of PM2.5–0.1 in Cork Harbour, Ireland. Atmos Res 95, 136–149. https://doi.org/10.1016/j.atmosres.2009.09.006.

Hoornaert, S., Moreton Godoi, R.H., Van Grieken, R., 2004. Elemental and single particle aerosol characterisation at a background station in Kazakhstan. J Atmos Chem 48, 301–315. http://dx.doi.org/10.1023/B:JOCH.0000044432.74476.b0.

IBGE, 2021. IBGE | Cidades@ | Paraná | Paranaguá | Panorama [WWW Document]. Instituto Brasileiro de Geografia e Estatística. URL https://cidades.ibge.gov.br/brasil/pr/paranagua/panorama (accessed 12.12.23).

ICCT, 2007. Air Pollution and Greenhouse Gas Emissions from Ocean-going Ships: Impacts, Mitigation Options and Opportunities for Managing Growth.

IMO, 2020. Introduction to IMO [WWW Document]. International Maritime Organization. URL https://www.imo.org/en/About/Pages/Default.aspx (accessed 12.12.23).

INMET, 2021. Inmet: Mapa de Estações [WWW Document]. Instituto Nacional de Meteorologia. URL https://mapas.inmet.gov.br/ (accessed 12.12.23).

Ji, C., El-Halwagi, M.M., 2020. A data-driven study of IMO compliant fuel emissions with consideration of black carbon aerosols. Ocean Engineering 218, 108241. https://doi.org/10.1016/j.oceaneng.2020.108241.

Kumar, A., Ambade,B., Sankar, T. K., Sehti, S. S., Kurwadkar, S., 2020. Source identification and health risk assessment of atmospheric PM2.5-bound polycyclic aromatic hydrocarbons in Jamshedpur, India. Sustainable Cities and Society 52, 101801. https://doi.org/10.1016/j.scs.2019.101801.

Lack, D., Lerner, B., Granier, C., Baynard, T., Lovejoy, E., Massoli, P., Ravishankara, A.R., Williams, E., 2008. Light absorbing carbon emissions from commercial shipping. Geophys Res Lett 35. https://doi.org/10.1029/2008GL033906.

Li, F., Yan, J., Wei, Y., Zeng, J., Wang, X., Chen, X., Zhang, C., Li, W., Chen, M., Lü, G., 2021. PM2.5-bound heavy metals from the major cities in China: Spatiotemporal distribution, fuzzy exposure assessment and health risk management. J Clean Prod 286, 124967. https://doi.org/10.1016/j.jclepro.2020.124967.

Liu, Q.T., Diamond, M.L., Gingrich, S.E., Ondov, J.M., Maciejczyk, P., Stern, G.A., 2003. Accumulation of metals, trace elements and semi-volatile organic compounds on exterior window surfaces in Baltimore. Environmental Pollution 122, 51–61. https://doi.org/10.1016/s0269-7491(02)00286-5.

Liu, X., Zhai, Y., Zhu, Y., Liu, Y., Chen, H., Li, P., Peng, C., Xu, B., Li, C., Zeng, G., 2015. Mass concentration and health risk assessment of heavy metals in size-segregated airborne particulate matter in Changsha. Science of The Total Environment 517, 215–221. https://doi.org/10.1016/j.scitotenv.2015.02.066.

Liu, X., Tian, Y., Xie, Q., Jia, B., Feng, Y., 2023. Contributors to reductions of PM2.5-bound heavy metal concentrations and health risks in a Chinese megacity during 2013, 2016 and 2019: An advanced method to quantify source-specific risks from various directions. Environmental Research 218, 114989. https://doi.org/10.1016/j.envres.2022.114989.

Lovett, C., Shirmohammadi, F., Sowlat, M.H., Sioutas, C., 2018. Commuting in Los Angeles: Cancer and Non-cancer Health Risks of Roadway, Light-Rail and Subway Transit Routes. Aerosol Air Qual Res 18, 2363–2374. https://doi.org/10.4209/aaqr.2017.09.0331.

Mamoudou, I., Zhang, F., Chen, Q., Wang, P., Chen, Y., 2018. Characteristics of PM2.5 from ship emissions and their impacts on the ambient air: A case study in Yangshan Harbor, Shanghai. Science of The Total Environment 640–641, 207–216. https://doi.org/10.1016/j.scitotenv.2018.05.261.

Marple, V.A., Rubow, K.L., Turner, W., Spengler, J.D., 1987. Low Flow Rate Sharp Cut Impactors for Indoor Air Sampling: Design and Calibration. JAPCA 37, 1303–1307. https://doi.org/10.1080/08940630.1987.10466325.

Masiol, M., Rampazzo, G., Ceccato, D., Squizzato, S., Pavoni, B., 2010. Characterization of PM10 sources in a coastal area near Venice (Italy): An application of factor-cluster analysis. Chemosphere 80, 771–778. https://doi.org/10.1016/j.chemosphere.2010.05.008.

Mason, B., 1966. Principles of geochemistry. Wiley.

Merk, O., 2014. Shipping Emissions in Ports [WWW Document]. International Transport Forum Discussion Papers. URL www.internationaltransportforum.org/jtrc/DiscussionPapers/jtrcpapers.html (accessed 3.28.23).

Moldanová, J., Fridell, E., Popovicheva, O., Demirdjian, B., Tishkova, V., Faccinetto, A., Focsa, C., 2009. Characterisation of particulate matter and gaseous emissions from a large ship diesel engine. Atmos Environ 43, 2632–2641. https://doi.org/10.1016/j.atmosenv.2009.02.008.

Mueller, L., Jakobi, G., Czech, H., Stengel, B., Orasche, J., Arteaga-Salas, J.M., Karg, E., Elsasser, M., Sippula, O., Streibel, T., Slowik, J.G., Prevot, A.S.H., Jokiniemi, J., Rabe, R., Harndorf, H., Michalke, B., Schnelle-Kreis, J., Zimmermann, R., 2015. Characteristics and temporal evolution of particulate emissions from a ship diesel engine. Appl Energy 155, 204–217. https://doi.org/10.1016/j.apenergy.2015.05.115.

NIOSH, 1994. CAS Number Listing - No CAS number - NMAM 4th Edition | NIOSH | CDC [WWW Document]. NIOSH 0500 Manual of Analytical Methods 881 (NMAM), Fourth Edition. URL https://www.cdc.gov/niosh/docs/2003-154/method-cas0.html (accessed 12.12.23).

OEHHA, 2012. Air Toxics Hot Spots Program Risk Assessment Guidelines. [WWW Document]. URL https://oehha.ca.gov/air/crnr/notice-adoption-technical-support-document-exposure-assessment-and-stochastic-analysis-aug (accessed 1.14.22).

Pandolfi, M., Gonzalez-Castanedo, Y., Alastuey, A., de la Rosa, J.D., Mantilla, E., de la Campa, A.S., Querol, X., Pey, J., Amato, F., Moreno, T., 2011. Source apportionment of PM10 and PM2.5 at multiple sites in the strait of Gibraltar by PMF: Impact of shipping emissions. Environmental Science and Pollution Research 18, 260–269. https://doi.org/10.1007/s11356-010-0373-4.

Park, M., Joo, H.S., Lee, K., Jang, M., Kim, S.D., Kim, I., Borlaza, L.J.S., Lim, H., Shin, H., Chung, K.H., Choi, Y.H., Park, S.G., Bae, M.S., Lee, J., Song, H., Park, K., 2018. Differential toxicities of fine particulate matters from various sources. Scientific Reports 2018 8:1 8, 1–11. https://doi.org/10.1038/s41598-018-35398-0.

Polezer, G., Oliveira, A., Potgieter-Vermaak, S., Godoi, A.F.L., de Souza, R.A.F., Yamamoto, C.I., Andreoli, R. V., Medeiros, A.S., Machado, C.M.D., dos Santos, E.O., de André, P.A., Pauliquevis, T., Saldiva, P.H.N., Martin, S.T., Godoi, R.H.M., 2019. The influence that different urban development models has on PM2.5 elemental and bioaccessible profiles. Scientific Reports 2019 9:1 9, 1–12. https://doi.org/10.1038/s41598-019-51340-4.

R Core Team, 2019. R: The R Project for Statistical Computing [WWW Document]. R Foundation for Statistical Computing, Vienna, Austria. URL https://www.r-project.org/ (accessed 12.12.23).

RAIS, 2022. The risk assessment information system [WWW Document]. URL https://rais.ornl.gov (accessed 1.14.22).

Rojas-Lemus, M.; López-Valdez, N.; Bizarro-Nevares, P.; González-Villalva, A.; Ustarroz-Cano, M.; Zepeda-Rodríguez, A.; Pasos-Nájera, F.; García-Peláez, I.; Rivera-Fernández, N.; Fortoul, T.I. 2021. Toxic Effects of Inhaled Vanadium Attached to Particulate Matter: A Literature Review. Int. J. Environ. Res. Public Health 2021, 18, 8457. https://doi.org/10.3390/ijerph18168457.

Saraga, D.E., Tolis, E.I., Maggos, T., Vasilakos, C., Bartzis, J.G., 2019. PM2.5 source apportionment for the port city of Thessaloniki, Greece. Science of The Total Environment 650, 2337–2354.https://doi.org/10.1016/j.scitotenv.2018.09.250.

Sarmiento, H., Potgieter-Vermaak, S., Borillo, G.C., Godoi, A.F.L., Reis, R.A., Yamamoto, C.I., Pauliquevis, T., Polezer, G., Godoi, R.H.M., 2023. BTEX profile and health risk at the largest bulk port in Latin America, Paranaguá Port. Environmental Science and Pollution Research 30, 63084–63095. https://doi.org/10.1007/s11356-023-26508-1.

Shetaya, W. H., El-Mekawy, A., Hassan, S. K., 2023. Tempo-Spatial Variability and Health Risks of PM2.5 and Associated Metal(loid)s in Greater Cairo, Egypt. Exposure and Health 2023, 1-16. https://doi.org/10.1007/s12403-023-00603-7.

Shi, Y., Zhu, Y., Gong, S., Pan, J., Zang, S., Wang, W., Li, Z., Matsunaga, T., Yamaguchi, Y., Bai, Y., 2022. PM2.5-related premature deaths and potential health benefits of controlled air quality in 34 provincial cities of China during 2001–2017. Environ Impact Assess Rev 97, 106883. https://doi.org/10. 1016/j.eiar.2022.106883.

SIMEPAR, 2020. Sistema de tecnologia e monitoramento ambiental do Paraná [WWW Document]. URL https://http://www.simepar.br/ (accessed 7.16.20).

Slaughter, A., Ray, S., Shattuck, T., 2020. International Maritime Organization (IMO) 2020 Strategies in a Non-Compliant World [WWW Document]. URL https://www2.deloitte.com/content/dam/Deloitte/us/Documents/finance/international-maritime-organization-pov-2020.pdf (accessed 7.3.22).

Sofiev, M., Winebrake, J.J., Johansson, L., Carr, E.W., Prank, M., Soares, J., Vira, J., Kouznetsov, R., Jalkanen, J.P., Corbett, J.J., 2018. Cleaner fuels for ships provide public health benefits with climate tradeoffs. Nature Communications 2018 9:1 9, 1–12. https://doi.org/10.1038/s41467-017-02774-9

Spada, N.J., Cheng, X., White, W.H., Hyslop, N.P., 2018. Decreasing Vanadium Footprint of Bunker Fuel Emissions. Environ Sci Technol 52, 11528–11534. https://doi.org/10.1021/ACS.EST.8B02942.

Tauchi, M., Yamaji, K., Nakatsubo, R., Oshita, Y., Kawamoto, K., Itano, Y., Hayashi, M., Hiraki, T., Takaishi, Y., Futamura, A., 2022. Evaluation of the effect of Global Sulfur Cap 2020 on a Japanese inland sea area. Case Stud Transp Policy 10, 785–794. https://doi.org/10.1016/j.cstp.2022.02.006.

UNCTAD, 2021. World Investment Report 2021: INVESTING IN SUSTAINABLE RECOVERY [WWW Document]. United Nations Conference on Trade and Development. URL https://unctad.org/system/files/official-document/wir2021_en.pdf. (accessed 7.3.22).

UNESCO, 1999. Atlantic Forest South-East Reserves - UNESCO World Heritage Centre [WWW Document]. United Nations Educational, Scientific and Cultural Organization. URL https://whc.unesco.org/en/list/893/ (accessed 7.3.22).

US EPA, 2015. Exposure Assessment Tools by Routes | US EPA [WWW Document]. US EPA NATIONAL CENTER FOR ENVIRONMENTAL ASSESSMENT, WASHINGTON DC, IMMEDIATE OFFICE. URL https://www.epa.gov/expobox/exposure-assessment-tools-routes (accessed 3.2.22).

US EPA, 2011. Exposure Factors Handbook 2011 Edition (Final Report) | Risk Assessment Portal | US EPA [WWW Document]. US EPA NATIONAL CENTER FOR ENVIRONMENTAL ASSESSMENT, WASHINGTON DC, IMMEDIATE OFFICE. URL https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=236252 (accessed 12.12.23).

US EPA, 2009. Risk Assessment Guidance for Superfund (RAGS), Volume I: Human health evaluation manual (Part F, supplemental guidance for inhalation risk assessment). [WWW Document]. US EPA NATIONAL CENTER FOR ENVIRONMENTAL ASSESSMENT, WASHINGTON DC, IMMEDIATE OFFICE.

Vedachalam, S., Baquerizo, N., Dalai, A.K., 2022. Review on impacts of low sulfur regulations on marine fuels and compliance options. Fuel 310, 122243. https://doi.org/10.1016/j.fuel.2021.122243.

Viana, M., Amato, F., Alastuey, A., Querol, X., Moreno, T., Dos Santos, S.G., Herce, M.D., Fernández-Patier, R., 2009. Chemical tracers of particulate emissions from commercial shipping. Environ Sci Technol 43, 7472–7477. https://doi.org/10.1021/es901558t.

Viana, M., Hammingh, P., Colette, A., Querol, X., Degraeuwe, B., Vlieger, I. de, van Aardenne, J., 2014. Impact of maritime transport emissions on coastal air quality in Europe. Atmos Environ 90, 96–105. https://doi.org/10.1016/J.ATMOSENV.2014.03.046.

Viana, M., Kuhlbusch, T.A.J., Querol, X., Alastuey, A., Harrison, R.M., Hopke, P.K., Winiwarter, W., Vallius, M., Szidat, S., Prévôt, A.S.H., Hueglin, C., Bloemen, H., Wåhlin, P., Vecchi, R., Miranda, A.I., Kasper-Giebl, A., Maenhaut, W., Hitzenberger, R., 2008. Source apportionment of particulate matter in Europe: A review of methods and results. J Aerosol Sci 39, 827–849. https://doi.org/10.1016/j.jaerosci.2008.05.007.

Wang, Y.F., Huang, K.L., Li, C.T., Mi, H.H., Luo, J.H., Tsai, P.J., 2003. Emissions of fuel metals content from a diesel vehicle engine. Atmos Environ 37, 4637–4643. https://doi.org/10.1016/j.atmosenv.2003.07.007.

Winebrake, J.J., Corbett, J.J., Green, E.H., Lauer, A., Eyring, V., 2009. Mitigating the health impacts of pollution from oceangoing shipping: An assessment of low-sulfur fuel mandates. Environ Sci Technol 43, 4776–4782. https://doi.org/10.1021/es803224q.

Zetterdahl, M., Moldanová, J., Pei, X., Pathak, R.K., Demirdjian, B., 2016. Impact of the 0.1% fuel sulfur content limit in SECA on particle and gaseous emissions from marine vessels. Atmos Environ 145, 338–345. https://doi.org/10.1016/j.atmosenv.2016.09.022.

Zhang, X., Eto, Y., Aikawa, M., 2021. Risk assessment and management of PM2.5-bound heavy metals in the urban area of Kitakyushu, Japan. Science of The Total Environment 795, 148748. https://doi.org/10.1016/j.scitotenv.2021.148748.

Zhao, M., Zhang, Y., Ma, W., Fu, Q., Yang, X., Li, C., Zhou, B., Yu, Q., Chen, L., 2013. Characteristics and ship traffic source identification of air pollutants in China's largest port. Atmos Environ 64, 277–286. https://doi.org/10.1016/j.atmosenv.2012.10.007.

Zhao, N., Elshareef, H., Li, B., Wang, B., Jia, Z., Zhou, L., Liu, Y., Sultan, M., Dong, R., Zhou, Y., 2022. The efforts of China to combat air pollution during the period of 2015–2018: A case study assessing the environmental, health and economic benefits in the Beijing-Tianjin-Hebei and surrounding "2 + 26" regions. Science of The Total Environment 853, 158437. https://doi.org/10.1016/j.scitotenv.2022.158437.

Zhu, T., Li, F., Niu, W., Gao, Z., Han, Y., Zhang, X., 2021. Health risk assessment of toxic and harmful air pollutants discharged by a petrochemical company in the Beijing-Tianjin-Hebei region of China. Atmosphere (Basel) 12, 1604. https://doi.org/10.3390/atmos12121604.