Chemical Tracers of Particulate Emissions from Commercial Shipping

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Despite the increase of commercial shipping around the world, data are yet relatively scarce on the contribution of these emissions to ambient air particulates. One of the reasons is the complexity in the detection and estimation of shipping contributions to ambient particulates in harbor and urban environments, given the similarity with tracers of other combustion sources. This study aimed to identify specific tracers of shipping emissions in a Mediterranean city with an important harbor (Melilla, Spain). Results showed that, for 24 h PM_{10} and $PM_{2.5}$ samples, valid tracers of commercial shipping emissions were ratios of V/Ni = 4−5 and V/EC < 2, whereas V/EC > 8 excluded the influence of shipping emissions. Other ratios (V/S, La/Ce, Zn/Ni, Pb/Zn, OC/EC) and tracers (Pb, Zn) were also tested but did not correlate with this source. Due to the changing composition of diesel fuels, tracers in the Mediterranean Sea may not be representative in other regions of the world and vice versa. The contribution of shipping emissions to ambient particulate matter (PM) urban background levels was quantified by positive matrix factorization (PMF), resulting in 2% and 4% of mean annual PM_{10} levels (0.8 $\mu g/m^3$ primary particles and 1.7 $\mu g/m^3$ secondary particles, with 20% uncertainty) and 14% of mean annual $PM_{2.5}$ levels (2.6 $\mu g/m^3$).

Introduction

Emissions from maritime ports and from shipping in general have significant environmental and human health impacts. Diesel engines on oceangoing vessels are significant contributors to air pollution in many cities and ports (*1*−*5*). Their emissions are expected to increase even more in the future due to the globalization of manufacturing processes and the increase of global-scale trade (*6*, *7*). However, this increased flow of commercial ships into and out of ports affects not only major ports but also medium and small-scale ones. The Mediterranean basin is characterized by atmospheric stagnation during the major part of the year, and consequently, shipping emissions accumulate on a regional scale. This is especially relevant along the Gibraltar Strait, as at this point ship traffic from the Mediterranean basin converges toward the Atlantic Ocean.

The link between particulate matter (PM) emissions from ships and health effects was recently assessed by Corbett et al. (*8*), who estimated that up to 60 000 premature deaths result annually. The primary reasons for the efficacy of shipping emissions to health are because 70% of shipping occurs within 400 km of land (*8, 9*) and major shipping ports are located in areas surrounded by large populations. The main source of PM from commercial shipping is diesel combustion. Marine diesel engines can burn a wide range of quality fuels, and they typically use the lowest cost fuels available. Thus, they use low volatility residual oil (commonly known as bunker oil), which is typically high in sulfur (∼2−5%) and porphyrins that contain Ni and V (*10, 11*) (average ash content of 0.072% (*11*)).

Diesel exhaust has been found to be of concern by several groups worldwide; urgent efforts should be made to reduce emissions, by changing exhaust emission abatement techniques, engine design, and fuel composition (*7, 12*). Different approaches are used in different countries to reduce shipping emissions; however, it has been acknowledged that actions to address these emissions have not yet achieved the goals for protecting human health (*7*). This derives mainly from the fact that identifying marine diesel PM in harbor areas and in coastal cities is highly complex, as is quantifying the contributions from this source to ambient PM levels. A relatively limited number of studies have attempted this quantification (*1, 10, 13*). There are various reasons behind this complexity:

- Large variability in fuel composition due to different engine types (heavy duty, light duty), engine operating conditions (idle, accelerate, decelerate), fuel formulations (high/low sulfur fuel), and distance to the coast (only high quality fuels are allowed while docking, as opposed to in open waters, even though this regulation is not always met). In addition, fuel composition changes rapidly, as it is highly dependent on cost.
- Similarity with tracers of other combustion sources: combustion sources using residual oil (e.g., power plants, refineries, etc.) generate emissions with characteristics similar to those from marine diesel engines.
- Absence of extreme PM episodes: unlike vehicular traffic, which has an episodic character showing high or low PM events (e.g., rush hour), ship traffic is frequent and mostly constant throughout the year. This constitutes a limitation for receptor modeling approaches, given that a large variability in the data is essential for the correct tuning of the models.
- Limited literature studies available: those available mostly refer to emission characterization (*2, 4, 11, 14, 15*).

The present study aims to identify specific chemical tracers of particulates emitted by commercial shipping, which will aid to overcome the difficulties described above to detect and quantify shipping contributions to ambient PM levels. Our work focuses strictly on shipping emissions, not those related to harbor operations (loading/unloading, handling, etc.).

The Mediterranean harbor at Melilla (1500−2000 ships/year according to the Melilla Harbour Authority, Figure 1) was selected for this study. The monitoring station was an urban background station located at approximately 150 m from the harbor and, thus, was strongly influenced by the emissions from docking ships, incoming and outgoing ships in the harbor itself, and ship traffic across the Gibraltar Strait.

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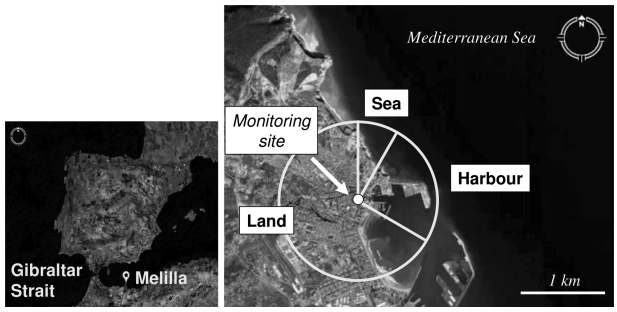

FIGURE 1. Location of Melilla and of the study site. Sea, harbor, and land: main wind sectors defined for the study.

Melilla is a medium-sized city (70 000 inhabitants, 13.4 km^2) with few major PM sources (road traffic, construction, harbor, a power plant). The meteorology in the area is dominated by alternating Easterly and Westerly winds, resulting in air mass flows originating from sea or from land, respectively. The main emission source reaching the study site under Easterly winds is ship traffic, both directly from the harbor and across the Gibraltar Strait (>82 000 ships/year (*16*)). The above considerations make the Melilla harbor an ideal location to study shipping emissions in the Mediterranean.

Experimental Methods

The monitoring station (35°17′33.06″ N, 2°56′12.99″ W, Figure 1) was located at approximately 15 m a.s.l. Sampling was carried out between January 2007 and April 2008, with 2 PM_{10} and 2 $PM_{2.5}$ 24 h samples per week (nominal start time 10:00 h UTC), collected on 15 cm diameter quartz fiber filters (Munktell) by means of MCV-CAV high-volume samplers (30 m^3/h). In total, 105 and 109 valid PM_{10} and $PM_{2.5}$ samples were collected, respectively. Mean hourly PM_{10}, $PM_{2.5}$, and PM_1 levels were also recorded using a GRIMM 1108 laser spectrometer, from January to December 2007 (approximately 25 000 data points collected). Correction factors were applied to the automatic data (1.03 for PM_{10}, 0.95 for $PM_{2.5}$ and PM_1), which were calculated by comparison with the reference gravimetric data. The average uncertainty of the automatic data ranged between 2 and 5 $\mu g/m^3$ (Table 1) and that of the gravimetric determinations was 1.5 $\mu g/m^3$ (*17*). Hourly wind speed and wind direction data were obtained from the Melilla reference network station (1 km from the monitoring site).

All filter samples were analyzed following the methodology in ref *18*, which determines the levels of 65 major and trace components. Levels of organic carbon (OC, uncertainty 0.2 $\mu g/m^3$) and elemental carbon (EC, uncertainty 0.1 $\mu g/m^3$) were determined by means of a thermo-optical technique with the EUSAAR2.par protocol (*19*). The uncertainties used in the receptor modeling analyses were calculated on the basis of Polissar et al. (*20*) and modified to include the measurement errors and the variability in the blank concentrations. Previous unpublished studies from our research team have proven the variability in blank concentrations to be rather large. On average, calculated errors ranged from 12% to 59% of the mass of all the variables.

Data on ship traffic into and out of the Melilla harbor were provided by the Melilla Harbour Authority. All incoming and outgoing ships were recorded on a daily basis, including data on ship size (length, depth, weight), type (cargo, cruise, passenger, etc.), flag, harbor of origin, etc.

Results and Discussion

Correlation between Ship Traffic and Monthly, Daily, and Hourly PM Levels. For the initial phase of the study, the aim was to detect the impact of shipping contributions on ambient PM levels. To this end, harbor data were processed and daily ship traffic data were obtained, in the form of total number of incoming/outgoing ships per day and also as a function of the type (mainly size) of ship. Mean monthly and daily PM levels were then plotted against ship traffic data, but no correlations were found for any of the size fractions analyzed (PM_{10}, $PM_{2.5}$, or PM_1, with $r^2 < 0.05$ in all cases). No increase in the monthly PM mean values was recorded with increasing ship traffic.

These results might be limited by the number of samples (342 daily samples), and thus, a similar analysis was attempted using mean hourly PM concentrations. In addition, hourly wind direction data were added to the analysis. Three main wind sectors were defined: open sea (0−45°), harbor (45−135°), and land (135−360°, Figure 1). Due to the characteristic meteorology of the region, dominated by the alternation of Easterly and Westerly winds, during the year 2007 on 94% of the sampling days, the winds originated from the East (45−135°) and West (225−315°), with Northern winds being recorded on only 5% of the days and Southern winds on 1% of the days. Thus, the influence on PM levels of the emissions originated by a fuel-oil power plant to the South of the monitoring site (<1 km distance) was considered minimal in this study.

In total, >8000 hourly data points were processed for PM_{10}, $PM_{2.5}$, PM_1 and wind direction, respectively. PM levels were plotted against wind direction data, and mean hourly PM levels were determined as a function of the wind sectors (Figure 1, Table 1). In this case, results showed marked differences between hourly PM levels coinciding with wind directions originating from sea (3187 data points) and from land (4363 data points), respectively. In addition, very similar PM levels were obtained from the open sea and harbor wind sectors (Table 1), suggesting that the shipping emissions registered in Melilla are not limited to the harbor, but they also represent the passing vessel traffic along the Gibraltar Strait. The analysis of the 20%ile and 80%ile confirmed the statistical significance of the mean hourly PM values obtained, given that these values register similar differences between wind sectors as the mean values and, thus, evidence that the variability in the mean values is not due to the presence of outliers.

Hourly PM levels were on average higher for all size fractions when the winds originated from the harbor and sea sectors than when winds originated from land, with differences of 7−9 $\mu g/m^3$ for PM_{10}, 5 to 6 $\mu g/m^3$ for $PM_{2.5}$, and 2 to 3 $\mu g/m^3$ for PM_1. These differences are larger than the uncertainty of the measurements, although relatively close to them. Because higher sea salt contributions could be causing the higher PM levels from the sea sectors, a specific analysis targeted toward this PM component was carried out. Results showed that similar contributions of sea salt aerosols were received from all wind sectors (0.9 $\mu g/m^3$ from the sea, 0.8 $\mu g/m^3$ from harbor and land), thus confirming that the above PM increments do not result from higher sea salt contributions. However, the origin of such PM increments cannot be directly linked to shipping emissions, given the potential influence of other PM sources and factors such as meteorology.

Potential Chemical Tracers of Shipping Emissions. A total of 12 major and 35 trace elements and components (see Querol et al. (*18*)) were determined in PM_{10} and $PM_{2.5}$. The $PM_{2.5}$ fraction was selected for this evaluation, given that these emissions are generally found in the smaller size fractions (*14*) and due to the availability of OC and EC determinations (for PM_{10}, only total carbon was available). Mean daily ratios between trace elements were calculated for the study period as a function of the three main wind sectors (sea, harbor, and land), and they were also correlated

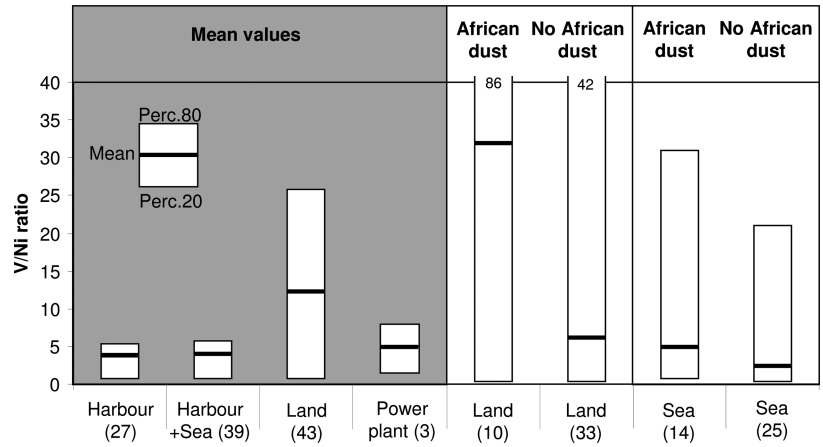

FIGURE 2. Mean V/Ni ratios in $PM_{2.5}$ as a function of four wind sectors: harbor, harbor + sea, land, and power plant. Data shown represent mean V/Ni ratios for the entire sampling period (left, on gray backgrund) and classified as a function of African dust periods (right, on white background). Perc 80: 80%ile. Perc 20: 20%ile. The number of data points is shown in parentheses on the *X* axis.

TABLE 1. Mean Hourly PM_{10}, $PM_{2.5}$, and PM_1 Levels as a Function of Three Main Wind Sectors Defined: Sea, Harbour, and Land[a]

	sea 0 < dir < 45			harbour 45 < dir < 135			land 135 < dir < 360		
	PM_{10}($\mu g/m^3$)	$PM_{2.5}$ ($\mu g/m^3$)	PM_1 ($\mu g/m^3$)	PM_{10} ($\mu g/m^3$)	$PM_{2.5}$ ($\mu g/m^3$)	PM_1 ($\mu g/m^3$)	PM_{10} ($\mu g/m^3$)	$PM_{2.5}$ ($\mu g/m^3$)	PM_1 ($\mu g/m^3$)
mean	46	22	14	44	21	13	37	16	11
perc 80	62	29	19	59	28	16	50	23	15
perc 20	26	13	8	28	13	8	23	9	6
uncert	5	2	2	5	2	2	5	2	2
n	1255	1255	1255	2562	2562	2562	4363	4363	4363

[a] Perc 80: 80%ile. Perc 20: 20%ile. *n*: number of data points. Uncert: uncertainty of the PM mass determination, calculated as the error in the correction of the automatic data with respect to the reference gravimetric data.

with ship traffic data (ship type and size). The following tracer ratios were evaluated:

- Vanadium/Nickel (V/Ni, numerous studies)
- Vanadium/Sulfur (V/S (*21*))
- Lanthanum/Cerium (La/Ce (*22*))
- Zinc/Nickel (Zn/Ni, based on Isakson et al. (*1*))
- Lead/Zinc (Pb/Zn, based on Isakson et al. (*1*))
- Organic carbon/Elemental carbon (OC/EC (*14*))
- Vanadium/Elemental carbon (V/EC, based on Fridell et al. (*14*))

Significant results were only obtained for V/Ni and V/EC ratios (see below). It is important to highlight that the remaining ratios (V/S, La/Ce, Zn/Ni, Pb/Zn, OC/EC) were tested but did not show correlations with shipping emissions and, thus, could not be considered as tracers, at this Mediterranean harbor (Figure S1, Supporting Information). However, due to the varying composition of particulates from shipping emissions around the world, certain of these tracers might be valid for other harbors (*1, 14*) (i.e., for Swedish harbors).

(a) Vanadium/Nickel ($(ng/m^3)/(ng/m^3)$). Figure 2 shows the mean daily V/Ni ratios as a function of wind sectors. Due to the lower number of samples (109 samples) when compared to the online PM data and to the lower frequency of the open sea wind sector, it was decided to merge the harbor and open sea sectors. This decision was based on the results above (Table 1) which suggest that the shipping contributions received in Melilla represent both the local harbor and the ship traffic across the Gibraltar Strait. Hourly wind direction data were not averaged to obtain daily values for the comparison with daily V/Ni ratios. Applying vector averaging resulted in a major loss of information given the characteristic meteorology of the study area, with rapidly changing winds (even within one day). To circumvent this limitation, each sampling day was classified into one of the main wind sectors based on the frequency of winds originating from each sector during a 24 h period. A threshold of 50% of the hours of the day was selected, e.g., the dominant wind direction for a given sampling day was classified as originating from the harbor sector, only if >50% of the hourly wind direction data for that day coincided with the direction of the harbor.

Results evidenced marked differences between daily V/Ni ratios obtained from the harbor and harbor + sea sectors (V/Ni = 4.0−4.1) and those obtained from land (V/Ni = 12.4). As in the case of mean hourly PM levels, the 20%ile and 80%ile demonstrated validity of these results by showing comparable values which exclude the possibility of the influence of outliers. The same analysis was also carried out for a specific wind sector including the fuel-oil power plant (150−225°), but results were not significant due to the limited number of data points ($n = 3$). Daily V/Ni variations were analyzed, and it was observed that the V/Ni differences between sea and land sectors could not be ascribed to systematically higher V levels from land or higher Ni levels from sea, but they resulted from combined fluctuations in V and Ni levels. In sum, it was concluded that for a Mediterranean harbor such as Melilla, a ratio of V/Ni = 4 may be considered as a tracer of particulate emissions from ships. This result is in accordance with the generally used ratio of V/Ni = 2.5−3 from ships and also specifically for the Mediterranean Sea (V/Ni = 3 was obtained under the influence of shipping emissions, a power plant, and an oil refinery (*23*)).

The high V/Ni mean ratio obtained for the land sector (V/Ni = 12.4) was further analyzed in order to understand its origin. In clay materials originating from African dust, it is known that V(III) may substitute Al(III) and, thus, the influence of soil dust could be incrementally changing the V/Ni ratio from the land sector. A separate analysis was carried

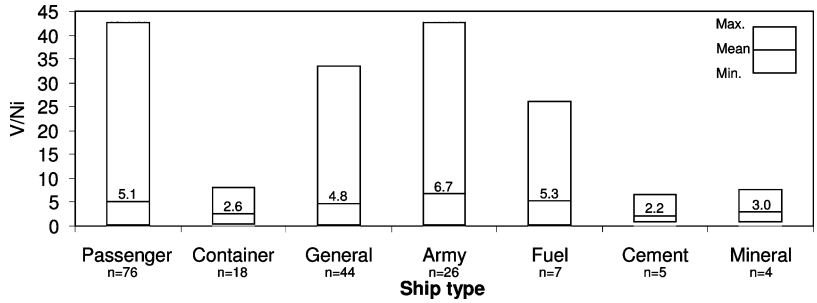

FIGURE 3. Mean, minimum, and maximum V/Ni ratios (in $(ng/m^{-3})/(ng/m^{-3})$) in $PM_{2.5}$ obtained for the different types of incoming and outgoing ships in the Melilla harbor.

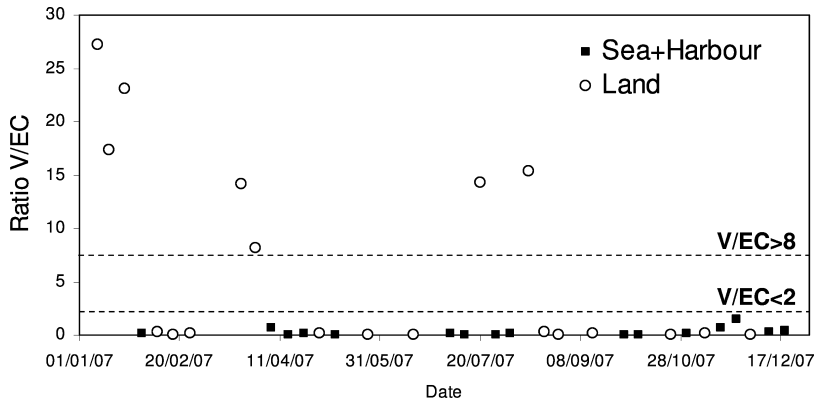

FIGURE 4. Mean V/EC ratios (in $(ng/m^{-3})/(\mu g/m^{-3})$) in $PM_{2.5}$ during the study period, as a function of the dominant wind direction (sea + harbor vs land).

out for the V/Ni ratio on days with and without African dust contributions, identified by back-trajectory analysis and interpretation of DREAM and NRL-NAAPS dust maps. A much higher mean V/Ni ratio was obtained from land for days with African dust (V/Ni = 32.0, Figure 2) than on days without these contributions (V/Ni = 6.0). Therefore, it was concluded that the high mean V/Ni ratio obtained from land resulted from the influence of African desert dust. When the same analysis was applied to the sea wind sectors, the mean V/Ni ratio showed a much smaller influence of desert dust (V/Ni = 2.5−3 on days without African dust, V/Ni = 5.0 on days with African dust) when compared to the mean values described above (V/Ni = 4.0−4.1).

The variability of this marker ratio was tested against the different types of ships in the Melilla harbor (Figure 3), aiming to detect possible differences which may allow for the identification of emissions from specific ships. These were classified according to the labels provided by the harbor authorities (e.g., passenger, fuel transport ships, etc.). Given that for each day various types of ships were always found in the harbor, the days were classified according to the prevailing ship type: if >50% of the ships in the harbor were of a certain type (e.g., passenger ships) then the day was classified as that type (e.g., "Passenger"). Mean V/Ni ratios were, thus, calculated for each day as a function of the ship type. The mean V/Ni ratios obtained ranged between 2.2 and 6.7, once more clearly distinct from the signal obtained from the land wind sector (12.4, Figure 2). A similar analysis was carried out classifying the ships as a function of their size: <5000 tons, 5000−10 000 tons, 10 000−15 000 tons, and >15 000 tons. However, no specific V/Ni ratios were derived for different ship sizes, and V/Ni ratios were still different from those characteristic of land emissions. Although, in this case, a slightly broader V/Ni range (3.9−8.4) was obtained.

(b) Vanadium/EC ($(ng/m^3)/(\mu g/m^3)$). Daily V/EC ratios were also evaluated. EC was considered a potential marker as it is emitted, in addition to in the shipping plume, in the form of re-entrained soot particles detached from walls in the engine systems (*14*).

Mean daily V/EC ratios were 0.4 for the harbor and sea wind sectors, and 5.4 for emissions originating from land. However, the detailed analysis of the daily V/EC values (Figure 4) evidenced that, as opposed to V/Ni ratios, the data were not evenly distributed (large impact of outliers) and, thus, the use of average values was not representative. However, V/EC ratios from the harbor and sea sectors were always <2, even though V/EC ratios from land emissions covered a wider range between 0.1 and 27.4. Thus, it was concluded that, in a Mediterranean harbor, V/EC ratios > 8 generally exclude the influence of shipping emissions, whereas V/EC < 2 may represent their influence. These results were also confirmed when taking the influence of African desert dust into account, given that ratios < 2 were always obtained from the sea. Higher V/EC ratios were obtained for days under the influence of African dust from land, due to the enrichment of desert dust in V.

V/EC ratios were also evaluated as a function of different ship types and sizes. The mean values obtained (0.1−3.8) showed larger deviations from the average value (0.4) for the sea and harbor wind sectors, when compared to the V/Ni ratio. These results were obtained both for varying ship types and sizes. Thus, V/EC ratios might differ as a function of the type of ships in the harbor, but a larger data set and further research would be needed in this direction.

(c) Correlations between Trace Elements: Lead (Pb), Zinc (Zn), Nickel (Ni), and Vanadium (V). The correlations between potential tracer elements were also assessed. In the Göteborg harbor (*1*) (Sweden), high positive correlations were obtained between NO, NO_2, SO_2, V, Ni, Pb, and Zn, which pointed toward their common origin in marine diesel exhaust. Correlation analyses were, thus, carried out for Melilla between Pb, Zn, Ni, and V, including SO_4^{2-} and NO_3^- as substitutes for gaseous pollutant data (unavailable in our study), for PM_{10} and $PM_{2.5}$, aiming to evaluate the validity for

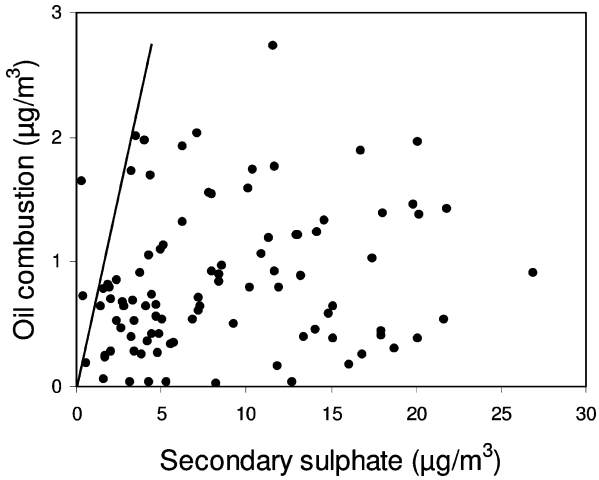

FIGURE 5. Correlation between the oil combustion and the secondary sulfate sources obtained by means of a PMF (positive matrix factorization) analysis.

a Mediterranean harbor of the tracers detected in Göteborg. Positive correlations ($r^2 > 0.4$) were only obtained between Ni and V in PM_{10} ($r^2 = 0.91$) and $PM_{2.5}$ ($r^2 = 0.87$) and between Pb and NO_3^- in $PM_{2.5}$ ($r^2 = 0.58$). However, the latter was interpreted as a tracer of traffic emissions, rather than shipping. This analysis was also carried out as a function of wind direction data, with similar results. Consequently, tracers of emissions from ships in Northern European harbors (e.g., Göteborg) may differ significantly from those in the Mediterranean Sea.

Quantification of Shipping Contributions to Ambient PM. Source apportionment analysis of the PM_{10} and $PM_{2.5}$ data were carried out by means of positive matrix factorization (PMF (*24*)), a receptor model with the fundamental principle that mass and species conservation can be assumed and a mass balance analysis can be used to identify and apportion sources of airborne PM in the atmosphere (*24*). Receptor models, including PMF, assess correlations between input variables and provide as output a number of factors which are interpreted as emission sources. Each of the output factors is characterized by a series of tracer elements, which aid to interpret the nature of the source. By means of multilinear regression analysis, the mean contribution of each of the sources to the total PM mass is calculated. In our case study, shipping emissions were detected as emission sources in PM_{10} and $PM_{2.5}$. The main tracers of this source in PM_{10} were total carbon, SO_4^{2-}, Ni, V, Cr, and Co, whereas in $PM_{2.5}$ they were Na, Cl^-, Ni, V, and Cr. Total carbon was used instead of OC and EC due to their low data availability (54% of the days).

For PM_{10}, six emission sources were identified by interpretation of their marker species: mineral matter (sum of two mineral sources accounting for 31% of the annual mean PM_{10} mass), road traffic (28%), secondary aerosols (24%), sea salt (15%), and shipping emissions (2%). Thus, the mass contribution of the shipping source was quite low (2% of PM_{10}, 0.8 $\mu g/m^3$). In addition, the variance of SO_4^{2-} explained by this factor was also strikingly low (5%, SO_4^{2-} being a tracer of secondary aerosols). As a result, this suggested that this source represented mainly primary particulate emissions from ships. Its main tracers were total carbon (expected to be mostly EC) and trace metals, all of which are tracers of primary emissions.

Based on these results, it is possible to calculate the secondary emissions associated to this source following this methodology (*10*), by correlating daily contributions from the primary shipping source with those from the secondary aerosol source obtained by PMF (Figure 5). The upper edge in this plot is a measure of the maximum amount of oil combustion particles (from shipping emissions) which are expected per unit contribution of secondary sulfate aerosols. The line marking the upper edge, as well as its slope, are calculated graphically and aim to exclude outliers. Thus, the slope of this line accounts for the maximum $\mu g/m^3$ of sulfate (secondary aerosol) corresponding to every $\mu g/m^3$ of oil combustion particles (primary aerosol). Given that NO_3^- is also usually present in the secondary aerosol factor, a correction needs to be applied to remove the NO_3^- contribution, and this was done by subtracting daily NO_3^- concentrations from the secondary aerosol source. In this way, a purely secondary sulfate source was estimated, which was then correlated with the oil combustion source. Despite the relatively low correlation obtained between both sources (Figure 5), the maximum contribution of secondary sulfate emissions was estimated to account for 1.7 $\mu g/m^3$ of the PM_{10} mass, with an uncertainty of 20% (0.3 $\mu g/m^3$). Consequently, the mean contribution of shipping emissions to ambient air PM in Melilla would account for 0.8 $\mu g/m^3$ (2% of the mean annual PM_{10}) as primary particles and 1.7 $\mu g/m^3$ (4% of PM_{10}, maximum value) as secondary particles (mainly sulfate aerosols from the oxidation of coemitted SO_2).

Regarding $PM_{2.5}$, a four-source solution was obtained, with the sum of primary and secondary particles from shipping accounting for 2.6 $\mu g/m^3$ (14% of the mean annual $PM_{2.5}$). This result coincides with the contribution obtained in PM_{10} (2.5 $\mu g/m^3$) within the error of the measurements and implies that shipping emissions are characterized by a fine grain size distribution ($PM_{2.5}$). Primary and secondary emissions could not be calculated as in PM_{10} due to the fact that no primary emissions factor was identified in $PM_{2.5}$. When compared with the relatively limited data in the literature, these values fall within the same range as the mean annual contributions to ambient $PM_{2.5}$ levels in Seattle (*10*) (1.2 $\mu g/m^3$), Los Angeles (*13*) (0.2−0.4 $\mu g/m^3$), and Algeciras (*23*) (Spain, 1.3 $\mu g/m^3$). Once again, the results obtained for the Mediterranean harbor in Melilla are interpreted as the sum of the emissions from ships in the harbor and those from passing vessels along the Gibraltar Strait.

As a conclusion of the present study, two valid tracers of commercial shipping emissions were obtained for Mediterranean harbors: (1) mean daily V/Ni ratios of 4 (ranging from 2.5−5) are markers of shipping emissions, and (2) mean daily V/EC ratios >8 exclude the influence of shipping emissions. Other tracers tested, but were not valid for Mediterranean harbors, were V/S, La/Ce, Zn/Ni, Pb/Zn, and OC/EC. In sum, the identification of marker elements or ratios of commercial shipping is a highly complex problem, depending on many variables of local character.

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Supporting Information Available

Figure S1 in Supporting Information shows the mean ratios in $PM_{2.5}$ of tracers which were tested but did not show correlations with shipping emissions and, thus, could not be considered as tracers, at this Mediterranean harbor (V/S, Zn/Ni, Pb/Zn, OC/EC, La/Ce). A receptor modeling analysis by means of the Multi-Linear Engine (ME) is available in this section. Figure S2 shows the results from the ME-2 fitting as a result of the progressive pulling of the V/Ni ratio toward values higher than two. This material is available free of charge via the Internet at http://pubs.acs.org.

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