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Detection and analysis of ship emissions using single-particle mass spectrometry: A land-based field study in the port of rostock, Germany

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ABSTRACT

The regulation of ship emissions has become more restrictive due to their significant impact on global air quality, particularly in coastal regions. According to the International Maritime Organization (IMO) regulations, current restrictions mainly limit the sulfur content of the fuel mass to 0.5 % and 0.1 % respectively. In compliance with these regulations, exhaust SO_2 cleaning systems (scrubbers) and new low-sulfur fuels are increasingly used. For comprehensive monitoring of ship emissions, advanced measurement techniques are demanded. Our study reports on the results of a land-based field campaign conducted in the port of Rostock, Germany. The chosen location strategically positions the measurement setup to capture all incoming and outgoing ships passing within a distance of up to 2 km. Potential ship exhaust plumes are indicated by rapid changes in particle number and size distribution monitored by an optical particle sizer (OPS) and a scanning mobility particle sizer (SMPS). Additionally, single-particle mass spectrometry (SPMS) was used to qualitatively characterize ambient single-particles (0.2–2.5 μm) by their chemical signatures. In a one-week time span, the exhaust plumes of 73 ships were identified. The high sensitivity of SPMS to transition metals and polycyclic aromatic hydrocarbons (PAH) in individual particles make it possible to distinguish between different marine fuels.

1. Introduction

Currently, more than 90 % of world trade is handled by global maritime transport, with a significant increase in trade volume projected for the upcoming decade. (European Commission. Directorate General for Climate Action. CE Delft, 2019) Maritime traffic releases substantial amounts of pollutants such as particulate matter (PM), carbon dioxide (CO_2), sulfur oxides (SO_x), nitrogen oxides (NO_x), and metals and thus contributes massively to global air pollution (Corbett et al., 2007; C. Geels et al., 2021; Mueller et al., 2023). Compared to road traffic pollution, emissions from ships are much less restricted and ships continue to emit high levels of pollutants, which has led to a gradual tightening of global regulations in the recent past.

In order to reduce emissions from ships and improve air quality, the International Maritime Organization (IMO) has progressively reduced the permitted sulfur content in fuels to a global level of 0.5 % fuel mass and 0.1 % in Sulfur Emission Control Areas (SECA). Many coastal regions and ports across the world, such as the entire North American coastal region, the North Sea, the Baltic Sea and all European Union (EU) ports, have been declared SECAs. Currently, the majority of ships operating in SECAs use approved low-sulfur fuels such as marine gas oil (MGO) or other modern fuels such as desulfurized blends of low-quality fuel (Lähteenmäki-Uutela et al., 2019).

Low-cost fuels such as heavy fuel oil (HFO) are still allowed to be used in SECAs, under the condition that gas aftertreatment equipment (so-called exhaust gas scrubbers) is installed which significantly reduces SO_2 emissions. The reduction of other pollutants, such as PM, however, is often insufficient (Fridell and Salo, 2016; Jeong et al., 2023). Thus, the impacts on the environment and human health remain high (Turner et al., 2017; Lunde Hermansson et al., 2021). Exhaust gas scrubbers are

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applied in closed-loop or open-loop mode. In both modes, large amounts of seawater are consumed. In contrast to the high efficiency of flue gas desulfurization, other gases and above all particulate emissions are hardly affected (Fridell and Salo, 2016; Jeong et al., 2023). In the more commonly used open-loop mode, the environmentally harmful residues are flushed directly into the sea.

Currently, numerous ships in SECAs, for example in the Baltic Sea, take advantage of the possibility to use low-cost, low-quality, and sulfur-containing fuels in combination with SO_2 scrubbers. The poor efficiency of scrubbers in relation to the particulate phase and their substantial long-term effects on the environment and human health makes further regulation highly desirable, especially in densely populated areas and sensitive ecosystems.

Compliance monitoring is essential and requires the large-scale use of advanced measurement technology. Routine measurements at monitoring sites on bridges or port entrances are usually based on gas phase measurements of CO_2 and SO_2 in exhaust plumes from passing ships (Kattner et al., 2015; Zhang et al., 2019; Krause et al., 2021), measurements with unmanned drones (Zhou et al., 2020a) or aircraft (Beecken et al., 2014) are also carried out, as are on-board sampling inspections (Lähteenmäki-Uutela et al., 2019).

Earlier studies point to the influence of fuel type on the physical and chemical properties of ship emissions (Streibel et al., 2017; Corbin et al., 2019) and their health effects (Winebrake et al., 2009; Oeder et al., 2015). Ship emission particles have very specific and source-related physical and chemical properties and can be transported over long distances by wind. This enables the analysis of PM from a distance of up to several kilometers with fixed or mobile measuring laboratories (Passig et al., 2021; Rosewig et al., 2023).

Particularly in areas with highly complex aerosols, as can be frequently observed in densely populated coastal regions, the detection methods for source apportionment can be relied on specific marker substances of ship emissions. As previous studies have shown, to detect ship emissions from heavy fuel oil combustion, the observation of combinations of the transition metals V, Fe and Ni is recommended (Pratt and Prather, 2012; Zimmermann and Hanley, 2021). Single-particle mass spectrometry (SPMS) is capable of detecting these metals in real time and has been used in several studies for land-based and marine on-board measurements to document air pollution from ships (Wang et al., 2019; Rosewig et al., 2023). In both laboratory and field studies, the combination of several ionization mechanisms has been successfully employed to analyze also particle-bound polycyclic aromatic hydrocarbons (PAHs) in ship emissions and use them to distinguish heavy fuel oil from distillate fuels (Czech et al., 2017; Anders et al., 2023).

In this study, we apply SPMS to detect individual ship exhaust plumes from a distance of a few kilometers in combination with standard measurement methods such as Scanning Mobility Particle Sizer (SMPS) and Optical Particle Sizer (OPS) which determine the size-related particle number concentration in the ambient air. And, therefore, are capable for rapid detection of ship exhaust plumes. It is shown, that combining these standard measurement methods with the analytical SPMS measurement system delivering a chemical characterization of individual particles in an exhaust plume, will be a powerful strategy for real-time compliance monitoring based on stationary on-shore measurements.

2. Materials and methods

2.1. Single-particle mass spectrometer

The SPMS measurement system employed in this field study was constructed based on a configuration engineered by Stefan Kaesdorf GmbH, similar to the first ground-taking architectures (Prather et al., 1994; Hinz et al., 1996). It includes two time-of-flight mass analyzers and uses aerosol time-of-flight mass spectrometry (ATOF-MS) technology. Detailed information on the functionality and the setup of the equipment used is provided in previous publications (Passig et al., 2017; Schade et al., 2019). A brief summary of the working principle is given here. The particles are introduced into the vacuum system of the MS through an aerodynamic lens prior to detection and size estimation by light scattering using a pair of Nd:YAG lasers (continuous wave, $\lambda =$ 532 nm) and photomultipliers. Subsequently, the particles enter the ionization chamber, where they are exposed to an infrared (IR) laser pulse (CO_2 laser, $\lambda = 10.6$ μm), inducing the desorption of polycyclic aromatic hydrocarbons (PAHs) from the particle surface. In the center of the ionization zone, the desorbed PAHs are ionized by the unfocussed beam of an UV laser (KrF excimer laser, $\lambda = 248$ nm) with moderate intensity (~3 $MWcm^{-2}$) via resonance-enhanced multiphoton ionization (REMPI). The laser beam is then reflected with a concave mirror, and the focused beam ionizes the residual of the particle in the focus with high intensity (~2 $GWcm^{-2}$) through laser desorption ionization (LDI). After a delay of 0.6 μs, all positive and negative ions are extracted and separately analyzed in two time-of-flight (TOF) mass spectrometers. This delayed extraction is implemented to enhance the resolution of mass spectra (Vera et al., 2005; Li et al., 2018). Both, the particle sizing information and the ion TOF spectra are recorded using a custom LabVIEW software.

2.2. Measurement site and aerosol sampling

The measurement instrumentation was installed inside a trailer and moved to the entrance to the port of Rostock on the German coast (54°10′14.8″ N 12°06′24.7″ E, Fig. 1). The trade and ferry port of Rostock is the largest German Baltic Sea port with an annual cargo throughput of >30 Mt and a passenger volume of >2.5 million. As the entire area of the Baltic Sea is a SECA, a sulfur limit of 0.1 % fuel mass applies to all shipping traffic. Although the compliance level is rather high (Lähteenmäki-Uutela et al., 2019), many ships, especially the Baltic Sea ferries, run on cheap heavy fuel oil and use sulfur scrubbers to remove the SO_2 from the exhaust gas (Magnusson et al., 2021).

The measurement site in close distance and east to the port entry (see Fig. 1) was chosen as an ideal location to monitor the large number of ships passing by daily, including cruise ships, ferries, cargo vessels, tankers and all other incoming and outgoing vessels within the port. Ship exhaust plumes are measured in the presence of a broad range of mainly downwind directions (northwest to southwest).

The ambient air was sampled at a height of 10 m.a.s.l. and distances to the passing ships of about 1 km. In order to collect a sufficiently high number of ship emission particles for SPMS analysis, a concentrator was used (model 4240, MSP Corp., Shoreview, MN, USA) (Romay et al., 2002) which concentrates the particles from a 300 L min^{-1} intake air stream into a 1 L min^{-1} carrier gas stream. The particles then pass through a dryer (model MD-700-12S-1, Perma Pure LLC, Lakewood, NJ, USA) and are finally concentrated again in a virtual impactor stage at the inlet of the SPMS right above the aerodynamic lens. According to the specifications of the concentrator and the single-particle MS, the focus of the analyzed single particles are in the size range of 0.25–2.5 μm (Su et al., 2004; Zelenyuk et al., 2009; Rosewig et al., 2023). A second sampling line, not connected to the concentrator, was operated with a standard setup for the measurement of the particle size distribution with SMPS and OPS (SMPS model 5420, OPS model EDM 180, both Grimm Aerosol Technik GmbH &Co. KG, Ainring, Germany). The SMPS was operated at a flow rate of 0.3 L min^{-1}, sheath flow of 3 L min^{-1}, 120 voltage steps and an up and down scan in a size range of 5–350 nm. The optical particle sizer (OPS) provided information on the number concentration of particles in the size range of 0.25–35 μm. In combination with the SMPS this enabled a total number concentration in the size range of 5–35.000 nm to be measured with a time resolution of 3 min.

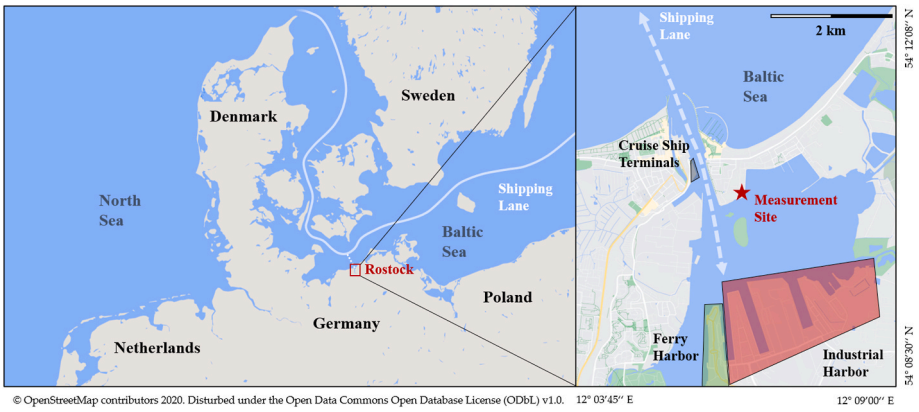

Fig. 1. The map section illustrates the location of the measurement site in the port of Rostock (Baltic Sea), the main shipping route, berths of Baltic Sea ferries, cruise ships as well as cargo and tanker ships in the industrial port.

2.3. Survey of data

This study focuses on measurement data recorded between July 11, 2022 and July 19, 2022. During this period of roughly one week, single-particle measurements as well as OPS and SMPS measurements were taken continuously throughout the day and night. Also, relative humidity, temperature, and air pressure were measured at the measurement site. Data on wind direction and wind speed were provided by the publicly available German Weather Service from a station in about 2 km distance west of the measurement site (https://opendata.dwd.de/climate_environment/CDC/observations_germany/climate/10_minutes/wind, station 4271, Rostock-Warnemünde, last access January 23, 2024). The air trajectories were calculated with the interactive web tool HYSPLIT of the GDAS model of the National Oceanic and Atmospheric Administration with a resolution of 0.25°(https://www.ready.noaa.gov/HYSPLIT.php last access March 12, 2024) (Stein et al., 2015).

2.4. Data analysis

All ship positions recorded by the AIS (Automatic Identification System) data logger during the monitoring interval within a radius of 25 km from the measurement site without restrictions on vessel characteristics were processed using in-house developed software based on the Matlab platform version R2023b (MathWorks Inc., Natick, MA, USA) to make it accessible for further analysis. Only fully transmitted data packages consisting of longitude, latitude, speed, course over ground, length, draught, name, MMSI (maritime mobile service identity), and vessel type were considered for use in this study. The data was sorted by the minimum distance to the measurement location, category and overall length of the vessels in order to identify the vessels of interest for this study. To trace the particle emissions of identified vessels, this position data was used in combination with meteorological data and the particle size distribution and particle mass concentration from the SMPS and OPS. For the qualitative on-line analysis of the ship particle emissions, the SPMS was utilized. For efficient post-processing of the data via ion marker screening, the raw data was processed into mass spectra of nominal mass resolution utilizing custom software on the Matlab platform.

3. Results

3.1. Ship movement data

During the measurement period, a total of 133 individual ships called at the port of Rostock and passed the measurement site at a distance of <2 km, 66 of which had an overall length of more than 75 m and were considered for the evaluation in this study. This group was subdivided according to category: cargo (35), passenger (19), tanker (7), and other (5). Most of the 61 ships identified as cargo, passenger, and tanker that called at the port of Rostock during the measurement period visited the port of Rostock more than once. Potential events were characterized by each passing of a ship at the measurement location, resulting in a minimum GPS distance between ship and measurement location. In total, 356 events of ships passing the measurement site during wind direction between 210 and 320° (southwest to northwest) were identified and studied, the majority of which were Baltic Sea ferries. For example, one of the ferries passed the measurement site 65 times during the recorded period. All in all, 259 potential events were caused by passenger ships, 75 by cargo ships and 22 by tankers (Table 1).

3.2. Particle data

During the measurement period July 11–19, 2022, the SMPS and OPS devices recorded the number of ambient air particles in the size range between 5 and 35,000 nm. A significant increase in the number of particles in the expected size range of PM may indicate a ship emission event (Lack et al., 2009; Diesch et al., 2013; Jeong et al., 2023), but additional information from the wind direction and AIS position data is required for a clear determination, since an increase in particle number can also be caused by a wide variety of other events.

During the same observation period, a total of 789,115 particles were detected and analyzed using SPMS. The mass spectra of these individual particles were examined using ion marker screening for classic ship emission markers. Mass spectra of bunker fuel (HFO) often show an increased signal intensity of the vanadium ion signal, especially in comparison to the iron or nickel ion signal (Healy et al., 2009; Ault et al., 2010; Rosewig et al., 2023). The SPMS is very sensitive to iron, as iron atoms have an absorption band at 248 nm, which corresponds to the wavelength of the applied KrF excimer laser (Passig et al., 2020).

In order to distinguish HFO particles from other particles from combustion engines, the ratio V/(V + Fe) and the increased signal intensity of the markers $^{51}V^+$ and $^{67}VO^+$ were observed (Healy et al., 2009; Ault et al., 2010; Passig et al., 2021). Other classic markers for

Table 1
Number of detected ship-passing events. 356 passages (259 passenger ships, 75 cargo ships, 22 tankers). were recorded using AIS receivers and SMPS + OPS particle counter devices. Analyzing the mass spectra (SPMS data), a total of 73 passages could be assigned to ship emissions.

	Passenger	Cargo	Tanker	Sum
AIS/SMPS	259	75	22	356
Detected by **SPMS**	55	15	3	73
HFO (high-sulfur fuel)	*44*	*15*	*3*	*62*
MGO (low-sulfur fuel)	*11*	*0*	*0*	*11*

HFO are an elevated $^{97}HSO_4^-$ and $^{80}SO_3^-$ ion intensity in the mass spectrum of negative ions and the presence of carbon clusters in both spectra. However, since an anthropogenic background as in the measurement location has also a high occurrence of carbon clusters, these markers were not considered in the evaluation.

Particles from MGO are much more difficult to distinguish from the anthropogenic background and that of other combustion engines. In recent studies it has been implied, that the increase of alkylated PAHs could indicate ship emissions, not just HFO, but MGO as well (Czech et al., 2017; Anders et al., 2023). Particles are identified as possible ship markers even in urban background if the *m/z* ratios of several alkylated PAHs (*m/z* = 192, 206, 220, and 242) are all above the mean value (Fig. 2 pink).

From the 356 ship passages recorded in the AIS data at southwestern to northwestern wind directions, observing the combination of the described signature markers in nominal mass spectra data, 73 events could be assigned to passing ships. Most of the detected events were ship emissions from heavy fuel oil combustion, but 11 events for MGO use were also detected (see Table 1).

4. Discussion

In SPMS measurements of airborne particles from ship emissions, different marker ions are used to identify emissions from different fuels. In many previous SPMS studies, as marker ions vanadium and vanadium oxide ($^{51}V^+$; $^{67}VO^+$) have been used and are well established (Murphy et al., 2009; Ault et al., 2010; Rosewig et al., 2023), especially for HFO combustion particles. Freshly emitted particles of ship emissions from HFO combustion additionally contain significantly higher amounts of sulfur than distillate fuel such as MGO, recognizable by the signals in the mass spectrum of the negative ions $^{97}HSO_4^-$, $^{81}HSO_3^-$ and $^{80}SO_3^-$ (Murphy et al., 2009; Ault et al., 2010).

For the identification and differentiation of emissions from bunker fuels and distillate fuels, the ratio between iron ($^{54/56}Fe^+$) and vanadium ($^{51}V^+$) signals can serve as a first indicator (Viana et al., 2014; Passig et al., 2021). Furthermore, the ratio of the parent PAHs to the alkylated PAHs can be used to identify emissions from shipping (Czech et al., 2017; Anders et al., 2023). When considering PAHs, however, a distinction can only be made between ship emissions and PAHs from other combustion processes and only to a limited extent between the different fuels. High signals for calcium ($^{40}Ca^+$) and calcium oxide ($^{56}CaO^+$), which can be identified as residues from the lubrication oil, are also characteristic for emissions from shipping (Shields et al., 2007; Toner et al., 2008).

To highlight the distinctions between two fuel types (HFO and MGO), four different averaged binary mass spectra are shown in Fig. 3 and will be discussed below.

Fig. 3(b) and c shows averaged mass spectra of particles from HFO combustion ship emissions. A reliable indicator for this type of fuel is the combination of the spectral peak intensities for V^+ and VO^+ ions, the ratio of V to Fe and the signal intensity of hydrogen sulfate ions. Ion signals for calcium, carbon clusters and PAH patterns serve as second-level discriminators. In contrast to the direct determination of ship emissions of HFO, particles from MGO combustion can only be identified indirectly by SPMS through the absence of first-level HFO markers and the simultaneous presence of second-level PAH markers (Fig. 3(a)).

The mass spectra essentially demonstrate high agreement with findings from previous studies, particularly regarding the first-level discriminators described above ($^{51}V^+$, $^{67}VO^+$, $^{40}Ca^+$, SO_3^-, HSO_4^-, carbon cluster) (Healy et al., 2010; Zhou et al., 2020b; Abou-Ghanem et al., 2024). (Of note, those studies used SPMS recordings when the regulations for emissions in SECA were less strict.) Differences could be identified in the signal intensity of $^{54/56}Fe^+$, which is generally stronger, in this application. This is due to the wavelength of the KrF excimer laser ($\lambda = 248$ nm) matching the absorption band of free iron atoms leading to their resonant ionization (Passig et al., 2020). In extension to previous field studies, signals for PAHs and organic molecules and molecule fragments could also be detected. This is due to the heating of the individual particles with a CO_2 laser ($\lambda = 10.6$ μm) and subsequent resonant ionization of PAHs ($\lambda = 248$ nm) (Passig et al., 2017; Schade et al., 2019).

Fig. 3(d) shows a mass spectrum that includes several of the first a second level markers, but shows clear differences in overall spectral pattern evaluation and shall therefore not be assigned to a ship exhaust plume.

As another illustrative example may serve the recordings in the time frame July 17 to July 18, 2022, 23:26–02:19 (Figs. S7 and S8). In this time frame, local authorities revealed and reported on a fire incident upwind (west-southwest) of the measuring station. In the particle plume, recorded during this time, strong signals of $^{35/37}Cl^-$, $ZnCl_3^-$, $^{206\text{-}208}Pb^+$ as well as various characteristic organic fragments could be found, which in the case of ship emissions do not occur in this combination, regardless which fuel type combustion emissions are considered.

Throughout the entire sampling period of roughly on week, 53,259 particles with an aerodynamic diameter <400 nm were detected by SPMS and showed an average aerodynamic diameter of about 250 nm. All of these particles were recorded during plausible ship passing events. This seems reasonable due to the typical size distribution of ship exhaust plumes (Lehtoranta et al., 2019; Jeong et al., 2023) and the short aging time of the particles, as the particles were emitted at a distance of less than 2 km.

With a measurement duration of 11,500 min, the average measurement frequency is ~5 particles per minute. With an average ship passing time and hence plume duration of 15 min, the number of particles

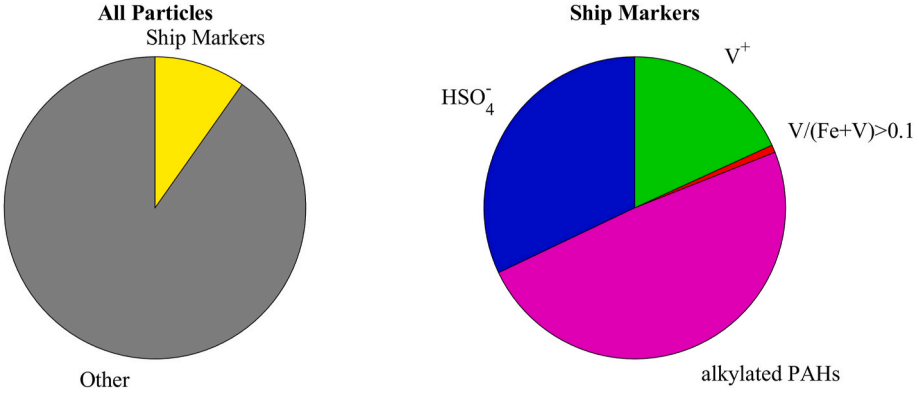

Fig. 2. On the left the distribution of all detected particle (789,115) mass spectra in two groups: ship markers (77,313 particles) and other (711,802 particles) is displayed. On the right there is the detailed distribution of particles with ship markers. Between $^{51}V+$ and $^{67}VO+$ enriched (green), $^{97}HSO_4$- enriched (blue), a ratio between V/(V + Fe) > 0.1 (red) and signals that are more intense than average for alkylated PAHs (m/z = 192, 206, 220, 242).

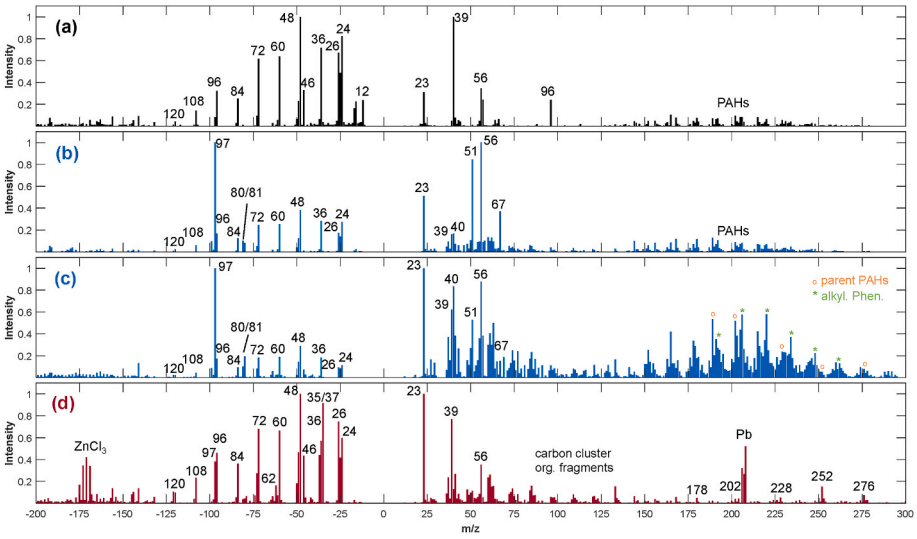

Fig. 3. Averaged bipolar mass spectra of single particles of labeled events in the size range below 400 nm. The peaks in the mass range m/z > 140 predominately originate from PAHs. (a) Averaged mass spectra indicating ship emissions from MGO combustion. (b) and (c) Mass spectra indicating ship emissions from HFO combustion. (d) Averaged mass spectra from a large fire incident upwind (west-southwest) of the measurement site in the night from July 17 to 18, 2022 (Figs. S7c and S8c).

measured per ship plume is 45 on average. For ship identification, a minimum number of 25 particles (>50 %) sized <400 nm and showing the above-mentioned ion markers was specified in this study. Plausible ship passing events were later confirmed manually based on the mass spectra.

Exemplarily, Fig. 4 shows the status of all mentioned indicators and – as a consequence - the identified ship emission events for an 8-h period (July 14, 2022, 05:00 to 13:00). Fig. 4(a) shows the dominant wind directions and velocities in 4-h intervals. Fig. 4(b) displays the particle numbers from the combined SMPS and OPS data (black line; scale on the right y-axis) and the time of detection and aerodynamic diameter of each particle detected by SPMS (scatter plot). Dark grey vertical lines in plot (b) indicate ship passages from AIS data, based on their minimal distance to the measurement site. The particle spectra were filtered based on typical ship emission markers: V^+ ions (green dots), peak ratio V/(V + Fe) > 0.1 (red dots), $^{97}HSO_4^-$ ions (blue dots), and higher-than-average peaks for the alkylated PAHs (m/z = 192, 206, 216, 220, 242) (pink dots). In the illustrated 8-h window, 9 emission events could be identified as corresponding to passing ships (oval boxes in Fig. 4 (b)).

A more detailed view of Fig. 4 shows that some of the emission-relevant particles detected by the SPMS are located after the vertical grey lines indicating the passage of a ship, based on the AIS data

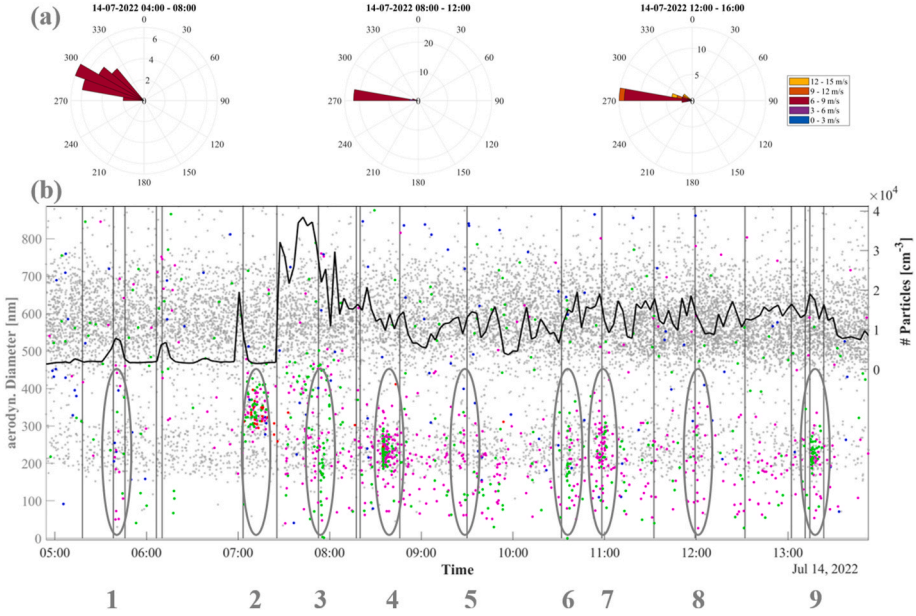

Fig. 4. Detection of ships from SPMS data with the according wind direction and speed. a) Representation of the wind speed and direction in 4-h intervals between July 14, 2022, 04:00 and July 14, 2022, 16:00 by wind roses. b) Plot of SPMS data between July 14, 2022, 05:00 and July 14, 2022, 14:00. Each particle spectrum obtained is represented by a grey dot based on the aerodynamic diameter. Particle spectra containing ship emission markers are represented by different colors: A V/(V + Fe) ratio >0.1 (red), elevated $^{51}V+$ and $^{67}VO+$ concentrations (green), elevated $^{97}HSO_4$- values (blue), and signals that are higher than average for alkylated PAHs (m/z = 192, 206, 220, 242) (pink). Based on the right y-axis, the SMPS data are shown in a black line. Dark grey vertical lines indicate a possible ship emission event from the AIS data. The areas enclosed by ovals indicate ship emission events based on SMPS data.

(passages 2,4,6, and 9). These time shifts between emission events observed in the mass spectra to the reported positions of ships relate mainly to the wind direction and velocity. Wind direction and, in particular, wind velocity influences the width of the particle plume. A comparison of AIS and SMPS data indicate that the particle plume generally reached the measurement site after a maximum of 15 min. A good indication for a particle plume from ship emissions is therefore given by the number of particles detected with SPMS and the specific markers in their mass spectra, accompanied by a significant particle concentration within the SMPS data in the same time frame of 15 min.

Interestingly, the time shifts between emission events observed in the mass spectra to the reported positions of ships relate also to the berth position, which in the Rostock port is different for the different ship types. The terminal for cruise ships, as a sub-category of passenger ships, is located north of the measurement site, see Fig. 1. Hence cruise ships do not pass the measurement site and the minimum distance to the measurement location is larger than that of the passing vessels, enlarging the travel time of the particle plume from their emissions.

For example, event 2 in Fig. 4(b) is likely to be an ocean-going cruise ship entering and anchoring in Rostock at the Cruise Ship Terminal: the wind direction was at 280° (northwest, as is the cruise ship terminal in relation to the measurement site), the mass spectra are characterized by a high number of particles with green and red dots for the significant markers for high vanadium ion concentration indicating the use of HFO in combination with an SO_2 scrubber. Events 5 and 8 are characterized by mostly alkylated PAHs (pink dots) and low amounts of first-level HFO markers which may be associated with MGO combustion emissions. Events 3,4,6,7 and 9 were most likely induced by ferries, which agrees with wind direction data (270°). Those events are generally characterized by first and second-level HFO markers and overall pattern evaluation. The ratios between alkylated PAHs and vanadium ion containing particles vary. It is noticeable that events 3 and 6 are primarily characterized by a sharp temporal sequence of V-containing particles and thus clearly differ from the other events. The particle spectra of both events are very similar and wind and AIS data confirm that the same passenger ship was detected entering and leaving the port.

After analyzing the SPMS data, from 356 recorded ship events for the observation period of about 8 days, 73 ship events were identified using the described identification method. Most of the mass spectra of the 73 identified events show increased vanadium ion signals in combination with alkylated PAHs, indicating that these ships were using conventional, cheap, and high-sulfur containing fuels with an SO_2 scrubber system. Our method, however, is not sufficient to infer significant differences in the emissions of different categories of ships (passenger, cargo, tanker), let alone to distinct between individual ships.

In Tables 1 and it is noticeable that only 3 of 22 tankers (13 %), but 15 of 75 cargo ships (20 %) were identified using SPMS. The difference is probably due to the primary wind direction and the different berth positions. Tankers berth is in the industrial port, to the southeast of the measurement site, while cargo ships and ferries berth southwest from the measurement site, see Fig. 1. During the measurement period, the main wind direction was westerly. Hence, the emission plumes of tankers were detectable by the SPMS for a much shorter time compared to cargo and passenger ships.

Our results clearly demonstrate the capabilities of the screening method of single-particle mass spectra. It should be noted, however that neither the appearance of the signature markers alone nor increased SMPS and OPC levels exclusively indicate ship events, as shown exemplarily in the supplement S7 and S8 (July 17 23:00 to July 18 00:30). Generally, background emissions from anthropogenic emission sources from car and rail traffic, industry and shipyards, or like in this case from fires, can have an influence on the measurements.

In summary, it became obvious that for reliable identification of emissions, a combination of indicators shall be observed, including SPMS, ion peak screening, and overall pattern recognition of the averaged mass spectra, particle numbers and size distribution (OPS, SMPS), ship movement data from AIS, and local wind measurements (direction and speed).

5. Conclusion

In order to monitor pollutant ship emissions in coastal areas, a measurement campaign was carried out during the period July 11–19, 2022, at the entry to the highly frequented ferry and cargo port of Rostock, Germany. With the combination of particle-counting devices (SMPS and OPS) and a single-particle mass spectrometer (SPMS), ship emission plumes of all incoming and outgoing ships in a distance of ~1–2 km from the measurement site were recorded and analyzed. The ship movements via AIS data logger and the wind movement data were also considered for the identification.

The differences in fuel batches and environmental influences such as humidity, temperature, wind direction and speed have a large influence on the chemical and physical properties of the particles detected. Within the scope of this study, roughly 20 % of all ships present in the port vicinity according to their AIS position data could be identified by their particle emission plume pattern.

It could be inferred from the particle measurements that the majority of larger ships of interest (ferries, cargo ships, tankers) run on cheap, but pollutant heavy fuel oil (HFO) and use SO_2 exhaust gas cleaners ('scrubbers'), which is mandatory in sulfur emission control areas (SECA) like the Baltic Sea.

Exploring the SPMS mass spectra, several conditions were set to discern ship plumes and hence ship passing events in the particle spectra: a plausible event is characterized by (1) >40 % particles indicating ship emission particles with aerodynamic diameters <400 nm detected (2) within a time frame of 15 min according to a passing ship known from its AIS position data, (3) a plausible wind direction and velocity (the measurement site was east of the port entry), (4) the presence of characteristic combination of marker ions in the mass spectra, and (5) overall pattern recognition and visual inspection. Using this strategy, a total of 73 events could be identified with high certainty and assigned to ships, out of 356 passages of ships of interest (passenger ships, cargo ships, tankers, that called at the port of Rostock; all with overall lengths >75 m). Analyzing the mass spectra of the emission plumes it was proven that in 62 detected passages of ships (72 % of all detected passages) high-sulfur HFO in combination with SO_2 scrubbers was used. Due to the better identifiability of ship emissions from HFO, this fuel type might be overrepresented in our results. However, the usage of scrubbers has risen sharply in the Baltic Sea. Most ferries use this technology and a large proportion of journeys in the port of Rostock are made by this type of ship. In the remaining cases the ships probably run on low-sulfur MGO, but this identification is more difficult due to less stable ion markers in the mass spectra and an absence of ion markers clearly differentiable from the anthropogenic background.

In summary, it could be shown on behalf of field measurements, that the combination of SMPS + OPS and SPMS is a universal and powerful observation method to distinguish particles from ship emissions from anthropogenic and natural background and even differentiate between different fuel types. Furthermore, we detected 11 ship passing events based on their pattern of alkylated PAHs in the absence of first-level HFO markers, which underlines the benefit of using alkylated PAHs in addition to the existing set of markers to reliably detect ship emissions, which are mainly connected to HFO emissions (Czech et al., 2017; Anders et al., 2023). The majority of mass spectra containing typical markers for ship emissions were from particles in a size range between 200 and 400 nm. These small sizes are attributable to freshly emitted particles from combustion engines showing low ageing of the particles. While the upper detection size limit is related to the short aging time of the air-transported particles, the lower limit is defined by instrumental specifications.

Important novel contributions to our investigations are longer-range detections of emission sources, to analyze aged particles from ship

emissions and to investigate the behavior of the marker substances for marine fuels, in particular alkylated PAHs. In order to perform the detection and analysis of ship exhaust plumes with higher accuracy and in an automated way, SPMS monitoring stations should be able to perform source attribution autonomously based on local weather data, online ship transponder data and plume dispersion models (Matthias et al., 2018; Badeke et al., 2021). Machine learning algorithms shall be used to evaluate the SPMS data by means of overall pattern evaluation (Wang et al., 2024).

CRediT authorship contribution statement

Ellen Iva Rosewig: Writing – original draft, Visualization, Formal analysis, Data curation. **Julian Schade:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Heinrich Ruser:** Writing – review & editing, Investigation, Funding acquisition. **Johannes Passig:** Resources, Funding acquisition. **Ralf Zimmermann:** Resources, Funding acquisition. **Thomas W. Adam:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.aeaoa.2024.100302.

Data availability

Data will be made available on request.

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