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Detection of Ship Plumes from Residual Fuel Operation in Emission Control Areas using Single-Particle Mass Spectrometry

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Abstract. Ships are main contributors to global air pollution with substantial impacts on climate and public health. To improve air quality in densely populated coastal areas and to protect sensitive ecosystems, sulfur emission control areas (SECA) were established in many regions of the world. Ships in SECAs operate with low-sulfur fuels, typically distillate fractions such as marine gas oil (MGO). Alternatively, exhaust gas cleaning devices ('scrubbers') can be implemented to remove SO_2 from the exhaust, thus allowing the use of cheap high-sulfur residual fuels. Compliance monitoring is established in harbors, but difficult in open water because of high costs and technical limitations. Here we present the first experiments to detect individual ship plumes from distances of several kilometers by single-particle mass spectrometry (SPMS). In contrast to most monitoring approaches that evaluate the gaseous emissions, such as manned or unmanned surveillance flights, sniffer technologies and remote sensing, we analyze the chemical composition of the particulate phase that is transported by the wind over long distances. We optimized SPMS technology for the evaluation of residual fuel emissions and demonstrate their detection in a SECA. Our experiments show that ships with installed scrubbers can emit PM emissions with health-relevant metals in quantities high enough to be detected from more than 10 km distance, emphasizing the importance of novel exhaust cleaning technologies and cleaner fuels. Because of the unique and stable metal signatures, our method is not affected by urban background. With this study, we establish a route towards a novel monitoring protocol for ship emissions. Therefore, we present and discuss mass spectral signatures that indicate the particle age, and thus the distance to the source. By matching ship transponder data, measured wind data and air mass back trajectories, we show, how real-time SPMS data can be evaluated to assign distant ship passages.

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1 Introduction

Among the variety of air pollution sources, ships emit particular large amounts of sulfur, carbonaceous aerosols and metals with substantial impacts on climate and public health (Corbett et al., 2007; Eyring et al., 2010; Viana et al., 2014; Jonson et al., 2020). Between 60,000 and 400,000 annual deaths by cardiopulmonary diseases and lung cancer as well as 14 million cases of childhood asthma were attributed to ship emissions (Sofiev et al., 2018). Mitigation strategies focus on the sulfur aspect, e.g. by a global 0.5% standard for ship fuels since 2020 and by implementation of Sulfur Emission Control Areas (SECA, <0.1% S in fuel mass since 2015) that currently comprise the Baltic Sea, the North Sea, and most of the U.S. and Canadian coast. Legal alternatives to the use of expensive distillate fuels in SECAs include desulfurized 'hybrid' blends of low-grade residual fuels (Lähteenmäki-Uutela et al., 2019) or the installation of exhaust cleaning devices for SO_2 like flue gas scrubbers (Winnes et al., 2018; Lehtoranta et al., 2019; Winnes et al., 2020).

Several studies investigated the effect of fuel composition on ship emissions and their respective effects on climate (Lack et al., 2011; Sofiev et al., 2018; Yu et al., 2020; Corbin et al., 2019) and health (Winebrake et al., 2009; Oeder et al., 2015). Beyond the SO_2 emissions, also the particle-phase pollution is specifically serious if low-grade heavy fuel oils (bunker fuels) are used (Moldanová et al., 2009; Sippula et al., 2014; Streibel et al., 2017; Di Wu et al., 2018). Within the various health effects of such combustion particles, specific risks for acute cardiovascular effects were associated with water-soluble fractions of particle-bound metals (Ye et al., 2018). Of note, iron solubility is promoted by the presence of sulfur (Fang et al., 2017), a situation that particularly arises for ship emission particles. Implementation of the sulfur regulations substantially decreased the use of residual fuels in SECAs (Jonson et al., 2019; Lähteenmäki-Uutela et al., 2019). However, of scrubber operation and combustion of desulfurized residual fuels reduce PM emissions only partially (Fridell and Salo, 2016; Lehtoranta et al., 2019; Winnes et al., 2020) and there is vital interest to assess the environmental and health effects (Winnes et al., 2018). Furthermore, compliance monitoring and emission inventories would benefit from the ability to distinguish between these options for ship operation.

Compliance monitoring on short distances is typically based on gas phase measurements of CO_2 and SO_2 in the plume of passing ships in harbors or at bridges (Kattner et al., 2015; Mellqvist et al., 2017b; Zhang et al., 2019). However, these places are known to be monitored, and also on-board checks occur frequently (Lähteenmäki-Uutela et al., 2019). Plume analyses in open water requires expensive surveillance flights (Beecken et al., 2014; Van Roy, W and Scheldeman, K., 2016). Unmanned aerial vehicles can reduce these costs but have limitations in cruising range and weather conditions (Zhou et al., 2020). Optical sensing technologies that have been utilized to monitor ship plumes on few-km distances comprise light detection and ranging (LIDAR), ultraviolet cameras and multi-axis differential optical absorption spectroscopy (MAX-DOAS) (Balzani Lööv et al., 2014; Seyler et al., 2017).

Monitoring techniques based on gas-phase measurements are limited in range because the gases rapidly mix with ambient air. In contrast, particles are transported by the wind over long distances. Field studies on particulate matter (PM) from ship plumes can be performed by following ships at some hundred meters to few kilometers distance (Chen, 2005; Lack et al., 2009; Petzold

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et al., 2008; Berg et al., 2012). A different approach to characterize ship plumes are stationary ambient measurements downwind of shipping lanes while recording the ship transponder data (Automatic Identification System, AIS). Recently, Ausmeel et al. measured physical and chemical properties of more than 150 ship plumes in the Baltic Sea from a distance of about 10 km (Ausmeel et al., 2019; Ausmeel et al., 2020). This method determines the presence of a ship plume by an increase in particle number and changes in its size distribution. Dispersion models of ship plumes showed rapid decrease in particle number concentration within the first minutes after emission (Tian et al., 2014). Therefore, particle number-based methods are restricted to low background levels and additional chemical indicators for ship plume presence may push the limits of stationary ambient measurements.

Established markers for aerosols from residual fuel combustion are combinations of vanadium, iron and nickel (Celo et al., 2015; Zhang et al., 2014). Single-particle mass spectrometry (SPMS) can detect these particle-bound metals in real time (Pratt and Prather, 2012; Passig and Zimmermann, 2021). Briefly, after optical sizing and introduction into vacuum, particles are exposed to intense UV laser pulses that form a microplasma (laser desorption/ionization, LDI). Both positive and negative ions are analyzed with respect to their mass-to-charge ratio (m/z). Thus, the size and a chemical profile from individual particles is obtained. SPMS studies documented air pollution by regional transport of emissions from harbors and shipping lanes (Reinard et al., 2007; Ault et al., 2009; Arndt et al., 2017; Gaston et al., 2013; Liu et al., 2017). Also individual ship plumes were analyzed by in-port studies (Healy et al., 2009; Ault et al., 2010; Xiao et al., 2018), demonstrating that SPMS can distinguish between residual fuel combustion and distillate fuel operation, predominantly by the metal signatures. All these studies were performed outside SECA zones, and, for the individual plume analyses, on short distances to the ships.

With the present study, we apply SPMS with resonant ionization of iron (Passig et al., 2020) for the detection of individual ship plumes from the distance to evaluate residual fuel combustion in SECA. We show that this approach is independent from background air pollution and we discuss the limits of detection over large distances. By examining indicators for particle ageing and the effects of inaccuracies in wind field determination, we pave the way to future open-sea monitoring of ship plumes using SPMS.

2 Experimental

2.1 Single-particle mass spectrometer and sampling

The SPMS was manufactured by Hexin Instruments Ltd., Guangzhou, China, and Photonion GmbH, Schwerin, Germany (Li et al., 2011; Zhou et al., 2016). It consists of a dual-polarity mass spectrometer in Z-TOF geometry (Pratt et al., 2009), an aerodynamic lens inlet and 75 mW continuous-wave lasers (wavelength λ=532 nm), ellipsoidal mirrors and photomultipliers for particle detection and sizing. The instrument is equipped with a KrF-excimer laser (λ=248.3 nm, PhotonEx, Photonion GmbH, Germany). The used wavelength is well-suited for resonance-enhanced laser desorption/ionization (LDI) of iron (Passig et al., 2020). Setting the lens (f=200 mm) to an off-focus position of 7 mm with respect to the particle beam, the spot size was about 150x300 µm and the resulting intensity 5 GW/cm^2 at 6 mJ pulse energy. The off-focus position in conjunction

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with the flat-top profile of the excimer laser beam allows hit rates around 50% (particles producing mass spectra vs. optically detected particles) (Schade et al., 2019; Passig et al., 2020).

Ambient air was sampled directly on the roof of the laboratory building (54°04'41.5"N 12°06'30.6"E), at a height of about 35 m above sea level. Because the study focuses on particles from distant sources, the sampling was optimized for larger particles ≳0.5 µm size at the expense of efficiency for smaller particles, such as local traffic emissions. Therefore, an aerosol concentrator, originally designed for particles above 2 µm size, was used (Model 4240, MSP corp., USA) (Romay et al., 2002). The multi-stage virtual impactor of this device concentrates particles from the 300 $L\,min^{-1}$ intake airflow into a 1 $L\,min^{-1}$ carrier gas stream, from which 0.1 $L\,min^{-1}$ were finally guided into the SPMS instrument. The real concentration factor for ambient air particles around 0.5 µm size was approximately 10:1, as estimated in previous experiments (Passig et al., 2020). Corrections of the inlet efficiency have not been applied.

2.2 Analysis of single-particle mass spectra

Using custom software on MATLAB platform (MathWorks Inc.), mass spectra were computed from time-of-flight data considering peak area within nominal mass resolution. Positive and negative mass spectra were separately normalized and missing negative ion spectra were set to zero. We classified the particles using the adaptive resonance theory neural network, ART-2a (Song et al., 1999) extracted from the open-source toolkit FATES (Flexible Analysis Toolkit for the Exploration of SPMS data) (Sultana et al., 2017) with a learning rate 0.05, a vigilance factor of 0.8 and 20 iterations. In short, positive and negative mass spectra of an individual particle are combined to one vector. Beginning with a randomly chosen spectrum, the inner products of every new spectrum with the weight vectors (already existing classes of particles) are calculated. The weight vector producing the highest inner product with the current particle is updated and the particle is assigned to this class, if the inner product exceeds the vigilance factor. Thus, the classes are iteratively adapted to the particle ensemble. If product is below this criterion, the current spectrum is considered as new weight vector (class).

Ion peak assignments corresponds to the most likely ion at a given mass (m/z). It should be noted, that SPMS obtains numbers of particles with particular chemical signatures, not the mass concentration of these components.

2.3 Meteorological and ship transponder data

The setup was housed in the southern periphery of the town Rostock (population 210,000) contributing urban background aerosols in between the sampling site and the coast**.** Possible regional aerosol sources comprise the urban area of Rostock, forests in north-eastern direction and farmland in the surrounding area, see Fig. 1.

Air trajectories were calculated using the interactive HYSPLIT web tool from the National Oceanic and Atmospheric Administration, model GDAS with 0.5° resolution (http://www.ready.noaa.gov/HYSPLIT.php, last access 10 November 2020) (Stein et al., 2015). Hourly wind data was obtained from the web archive of a local meteorological station that belongs to Germany's National Meteorological Service, 12 km north of the sampling site and close to the harbor exit (https://www.dwd.de/DE/leistungen/klimadatendeutschland/klarchivstunden.html#buehneTop, last access 12 November

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2020). AIS data for all ships sailing between 54°N, 11.5°E and 55.5°N, 16°E in the measurement period (26 June – 2 July 2018) was acquired from the German Federal Waterways and Shipping Administration in anonymized form, analyzed and filtered by custom software on Matlab platform. Small vessels below 60 m length were excluded.

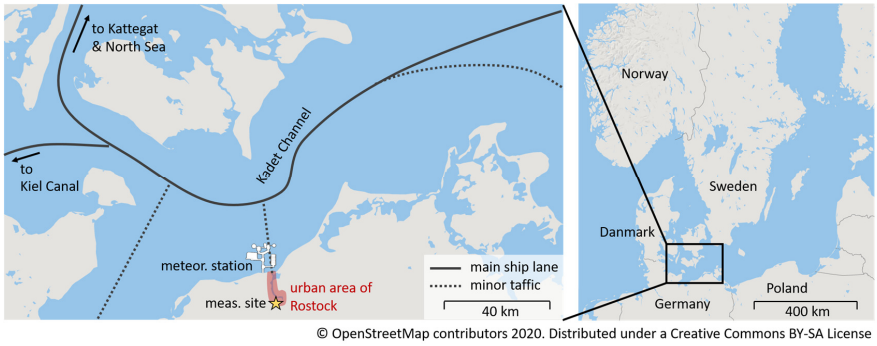

Figure 1: Overview map of the region illustrating the major ship lanes and the position of the measurement site and the meteorological station providing the wind data. A more detailed map can be found in Fig. 6.

3 Results and Discussion

Before focusing on particles from residual fuel combustion, we characterize the overall particle ensemble and meteorological situation that represent a typical scenario for a North-European coastal region during summer.

3.1 Main particle classes

During 26 June – 2 July 2018, a total number of 290,144 particles were detected by the SPMS instrument, 162,288 particles yielded mass spectra and were sized and chemically analyzed. The ART-2a algorithm produced 715 particle clusters, whereof the top 300 clusters accounting for >90 % of the particles were visually inspected. Similar clusters, based on the ion signal of key species were grouped by hand into six general categories. Such groups have variations among their clusters, but similar signatures of the same overall chemical species as well as comparable temporal trends and size distributions. The labelling scheme reflects the most intense peaks and characteristic species for the respective general particle type and is frequently used in the literature (Ault et al., 2010; Decesari et al., 2014; Dall`Osto et al., 2016; Arndt et al., 2017). Peaks are assigned with respect to the most probable ions for a given m/z ratio. The mass spectral signatures of all 300 inspected clusters as well as time series of their particle counts are provided in the Supplement, the attribution to general classes is documented by Table S1.

Six general particle types were identified. Their particle number and aerodynamic size can be found in Fig. 2(a), whereas average mass spectra of anions and cations are shown in Fig. 2(b) and (c), respectively. Carbon-containing particles contributed the majority to total particle numbers. Their spectra are either dominated by strong carbon cluster peaks from elemental carbon

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(EC), or by molecular fragments from organic carbon (OC). The balance between these signatures indicate the EC/OC ratio (Ferge et al., 2006; Spencer and Prather, 2006), however, in the present study this ratio is a continuum, broken into several small clusters by ART-2a (Zhou et al., 2006) and manually merged according to their dominant signals.

The EC-OC particle class shows no distinct K^+ peak, indicating fossil fuel combustion (oil burning or traffic) as most likely source. It has been shown that secondary material increases the particle's hygroscopicity (Moffet et al., 2008)(Ault et al., 2010; Decesari et al., 2014), suppressing the formation of negative ions (Neubauer et al., 1998; Hatch et al., 2014). The strong sulfate signal and the frequent absence of negative carbon clusters indicate condensation of sulfate during atmospheric transport, while its dominance over nitrate can result from processing in marine environment (Ault et al., 2010; Köllner et al., 2017), but also from the summer weather conditions due to the higher volatility of ammonium nitrate compared to ammonium sulfate (Querol et al., 2009; Arndt et al., 2017).

Particles with molecular fragment signals dominating over the carbon clusters were assigned to the OC-EC class. They also show a pronounced K^+ peak and nitrogen-containing signals; both can be attributed to a higher contribution of biomass combustion (Silva et al., 1999; Pagels et al., 2013).

In the K-CN class, K^+ signals dominate the cation mass spectra, a well-documented signature for aerosols from biomass burning and wood combustion (Silva et al., 1999; Zhang et al., 2013). Potassium has a low ionization energy and the ion is energetically preferred compared to ions of other species, thus it survives collisions in the particle plume, when other ions are neutralized (Reinard and Johnston, 2008). The mass spectra of negative ions show CN^- and CNO^- signals from nitrogen-containing organic compounds (Silva et al., 1999; Köllner et al., 2017).

A particle class similar to the K-CN particles, but with higher peaks from NO_2^- and NO_3^- indicate a strong contribution of secondary material, including nitrate in addition to the sulfate.

Sea salt particles are typically larger and produce characteristic signatures. Fresh sea salt particles are characterized by sodium ions (e.g. $^{23}Na^+$, $^{46}NaC^+$, $^{62}Na_2O^+$, $^{63}Na_2OH^+$), K^+, $^{16}O^-$ and $^{35,37}Cl^-$. (Dall'Osto et al., 2004; Murphy et al., 2019). Chlorine is replaced by nitrate during atmospheric processing (Gard et al., 1998), thus the strong nitrate signals and weak chlorine peaks ($^{35,37}Cl^-$) suggest that these particles are not fresh but have been transported over some distance.

The combination of signals from the transition metals V, Fe and Ni is a well-documented marker for particles from residual fuel combustion on ships (Healy et al., 2009; Ault et al., 2010; Xiao et al., 2018; Furutani et al., 2011; Reinard et al., 2007). The peak relative intensities do not reflect the mass concentration of these species and further metals such as Zn and Cu are less frequently detected in SPMS, despite their high concentration in the fuels and particles (Viana et al., 2009; Popovicheva et al., 2012; Moldanová et al., 2009; Streibel et al., 2017; Corbin et al., 2018). The mechanisms and interactions that affect the ion formation in LDI are not understood in full detail (Reinard and Johnston, 2008; Hatch et al., 2014), however, recently we could show that the light absorption of free atoms in the particle plume can play an important role (Passig et al., 2020). In previous studies on ship emissions, Vanadium signals dominated largely over Fe and Ni peaks (Healy et al., 2009; Ault et al., 2010), and were partly treated as a singular marker (Xiao et al., 2018). However, particularly in an ion marker-based approach, $^{51}V^+$ and $^{67}VO^+$ can interfere with major organic fragments (and $^{56}Fe^+$ with $^{56}CaO^+$). Of note, the KrF-excimer laser used in

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our experiment resonantly ionizes particle-bound Fe, enabling a more efficient and secure detection of iron (Passig et al., 2020). This allows us to strengthen the assignment by counting only particle clusters to the V-Fe-Ni class that show either the complete peak pattern of $^{51}V^+$, $^{56}Fe^+$, $^{58}Ni^+$, $^{67}VO^+$ or $^{51}V^+$, $^{54}Fe^+$, $^{56}Fe^+$, $^{67}VO^+$. Beyond the transition metals from residual fuel combustion, the V-Fe-Ni particles reveal Ca^+ ions that can be attributed to additives of lubrication oil (Toner et al., 2006; Spencer et al., 2006), minor signals from EC and OC as well as a particularly intense $^{97}HSO_4^-$ peak. Considering that also the other particle classes show a strong $^{97}HSO_4^-$ signal, the sulfate can be primary and secondary.

Apart from the aged sea salt, the particles of all classes show comparable sizes, see Fig. 2(a). One explanation lies in the instrumental setup: The optical detection of particles based on Mie scattering is most effective for particle sizes that roughly match the laser wavelength (here 532 nm) and drops rapidly below about 150 nm (Gaie-Levrel et al., 2012). The aerosol concentrator is optimized for particles of about 2.5 – 10 µm size (Romay et al., 2002) and most likely ineffective for particles smaller than 0.5 µm. While detailed data on its performance for small particles is not available, we could estimate an approximately ten-fold concentration for 0.5 µm particles in a previous study (Passig et al., 2020). Beyond the instrumental aspect, particles in the accumulation mode have the longest residence time in the atmosphere and are transported over large distances (Seinfeld and Pandis, 2016). They can dominate the size distribution in remote areas, and also if local emissions are of minor importance or if they rapidly grow, e.g. by condensation of secondary material.

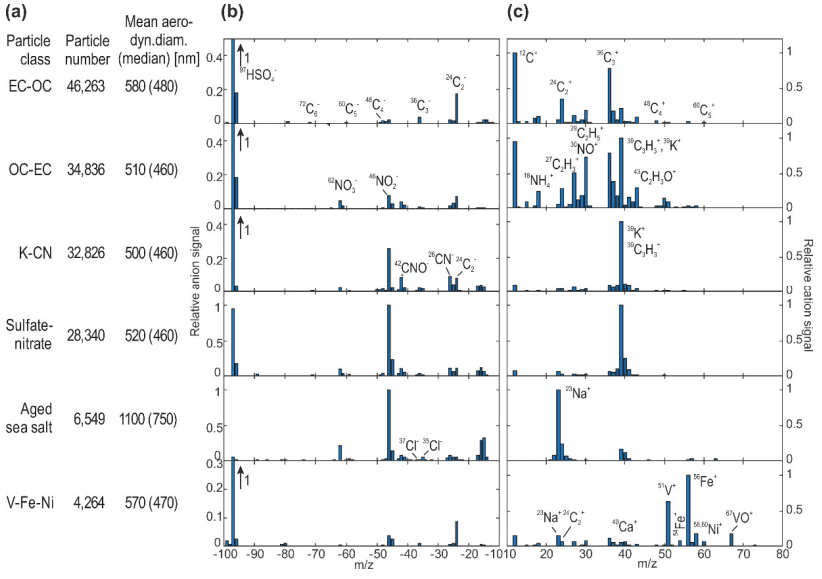

Figure 2: (a) General particle classes, their respective particle numbers and aerodynamic size. (b) Average anion mass spectra and (c) cation mass spectra of the particle classes. The mass spectra of the top 300 particle clusters from ART-2a analysis are shown in the Supplement and their assignment to the general classes is documented by Table S1.

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205 **3.2 Time series of main particle classes and air mass history**

The measurements were performed during a period of relatively calm summer weather with light to moderate winds from mostly northern to eastern directions. The mean PM 2.5 mass was 4.0 µg/cm^3 and the mean particle number density was 44 cm^{-3} (0.25–32 µm), as measured by a monitoring station near the coast line (Grimm EDM-180, http://www.lung.mv-regierung.de/umwelt/luft/akt_wahl.htm). In order to improve the clarity, Fig. 3(a) lists the regions passed by the air masses
210 within the last 24h before arriving at the sampling site, while the detailed back trajectories are shown in Figs. S2 and S3 Most of the trajectories passed open sea and sparsely populated regions before reaching the nearby coastal waters and finally the sampling site. The last hour of the trajectories before arriving at the site can be determined from the local wind data, recorded at the coastline 12 km north of the site, see Fig. 3(b). After crossing the heavily trafficked ship lanes >20 km north off the coast (see Fig. 1) the air enters the site either directly from the north passing the urban area of Rostock, or from eastern directions
215 passing rural regions with forests and agricultural areas.

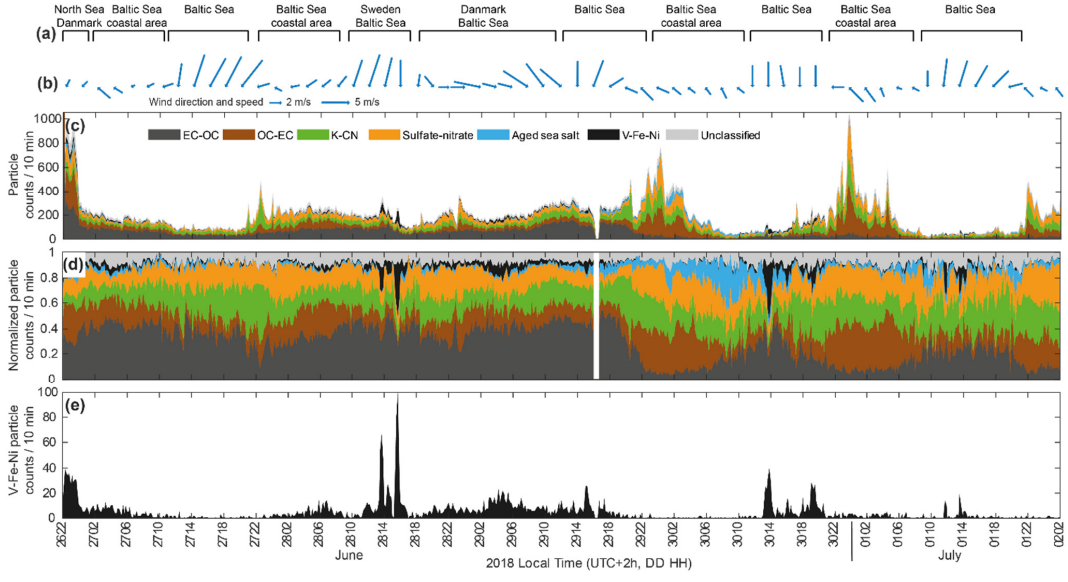

Figure 3: (a) Air mass origin (top row: >12 h, bottom row <12 h) according to the HYSPLIT back trajectory analysis (Fig. S2 and S3). (b) Measured wind data from the meteorological station at the harbor exit, 12 km north of the measurement site. (c) The time
220 **series of particle counts from the general particle classes shows regional/long-range transported air pollution (26-29 June) and night-time secondary organic aerosol formation (29 June – 02 July). (d) The same data as (c), but normalized to total particle counts illustrate the contribution of each particle type as well as increased sea-salt levels during the 30 June. (e) The temporal behavior of V-Fe-Ni particles from residual fuel combustion reveals transient events and smooth background signals, predominantly during onshore winds. Apart from the short events, their contribution to total particle numbers is low.**

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The wind data (Fig. 3(b)) reveal a pronounced land/onshore circulation, with regularly northern winds in the afternoon and light winds from different directions in the night and morning hours. Fig. 3(c) shows time series of the particle numbers within the general particle classes, while Fig. 3(d) shows their relative contribution to total particle numbers, both with 10 min resolution.

The EC-OC particle numbers (dark grey area) exhibit a weak diurnal oscillation, however, not with enhanced levels during the morning and afternoon as expected from increased local traffic and human activity. In contrast, they follow the changes in wind direction and speed. It is conceivable that the northern winds transport local emissions from the city center to the sampling site, however, the strong sulfate peaks in the EC-OC group and the lack of negative ions point on aged particles that might have been transported over larger distances, see Fig. 2. Also the particle size is larger than typical for urban traffic emissions (Dall`Osto et al., 2016) which is in agreement with the assumption that these freshly emitted particles are underrepresented compared to the larger ones that are enriched by the aerosol concentrator.

The OC-EC-, K-Cn and Sulfate-nitrate particles roughly follow the trend of the EC-OC particles, but show an additional diurnal variation that is especially pronounced during the last two days of the measurements. Their particle numbers increase after sunset and drop in the morning, reflecting condensation of semi-volatile components at night. This temporal behavior is comparable for OC-EC, K-CN and Sulfate-Nitrate particles, because: (I) They are all composed of organic matter to some extend. (II) They can simultaneously grow into the efficiently detected size mode by condensation of secondary material, and (III) all possible diurnal features of aerosol chemistry, such as daytime photochemical formation of SOA or increases in nitrate with relative humidity (Salcedo et al., 2006; Dall'Osto et al., 2009; Healy et al., 2012) are interfered by the strong land/onshore circulation. This dominance of air circulation over local atmospheric chemistry is also reflected by the pronounced particle number maxima during the last nights of the measurement period, where local terrestrial air masses contribute. In contrast, during the second and third night, the air trajectories passed over less land before entering the site and the maxima are substantially smaller. Also the OC-EC and K-CN particle numbers follow the diurnal trend, probably because they grow by night-time condensation into the size mode that is enriched by the aerosol concentrator, while local emissions of smaller particles are barely detected. However, a small transient feature of K-CN particles can be noticed at the 29th June at 8 pm, before the general increase after sunset around 10 pm. It might be associated with local emissions, e.g. from barbecuing. The enhanced contributions of aged sea salt at the 30th June can be attributed to stronger winds in the central Baltic Sea.

The time series of V-Fe-Ni particles (Fig. 3(e)) resembles the temporal profile of the ECOC particles, however, with additional transient features. These features have a width of approximately 20–60 min and occur only during wind from the North. As apparent from Fig. 3(d), the V-Fe-Ni contribute only a small fraction to total particle numbers, however, during the transient events these contribution accounts for 10–20 %.

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3.3 Chemical and temporal profiles of residual fuel emission particles

In order to elucidate the sources and atmospheric processing of the V-Fe-Ni particles, we separately analyzed the mass spectra and temporal behavior of 12 out of the total 15 clusters that were combined to the V-Fe-Ni class. Fig. 4(a) lists the clusters according to their labels in the full cluster analysis (1st row in Fig. 4(a), see Supplement) in the order of their respective particle numbers (2nd row). The mass spectra (Fig. 4(b) and (c)) show signals from EC, OC, Ca^+ and Na^+, see section 3.1 as well as the metal signatures that were used as markers for residual fuel combustion. Generally, all clusters with negative ion spectra reveal a dominant $^{97}HSO_4^-$ peak (with additional EC signals for cluster 161 and 164 and nitrate for cluster 226).

3.3.1 Background particles and particles from transient events

Time series of the particle clusters are depicted in Fig. 4(d). An important finding here is that the cluster algorithm was exclusively applied to chemical particle data, but it also yielded two distinct groups according to the particle's temporal behavior, as discussed in the following.

The first group of V-Fe-Ni particles, comprising the clusters 97, 111, 127, 138, 196 and 226 shows rather smooth time series, comparable to the EC-OC class in Fig. 2(c). The mass spectra of his group reveal either no negative ions or comparable small signals from sulfate (4th row in Fig. 4(a)) or secondary nitrate (cluster 226). Also, the positive ion signals apart from transition metals are weak. The smooth temporal behavior (Fig. 4(d)) gives rise to the term 'background group'. These particles are predominantly observed during phases of light on-shore winds, also from North-Western directions, where heavily trafficked ship routes towards the North Sea and the Atlantic Ocean are located. Such particles most likely origin from distant sections of the shipping lanes or distant regions.

The second group identified by mass spectral signatures contributes the transient events and is formed by the clusters 110, 150, 151, 161, 164 and 183. All of these particle clusters show negative ions and, with the exception of cluster 150, also remarkable signals of EC, OC, Ca^+ and Na^+ in the positive ion mass spectra. We term these particles the "transient group", as their temporal behavior point on individual, less distant sources. Cluster 111 combines both properties. Because of the biased aerosol concentration and sampling in our study, the particle size distribution is rather uniform and allows no differentiation between local and distant emissions.

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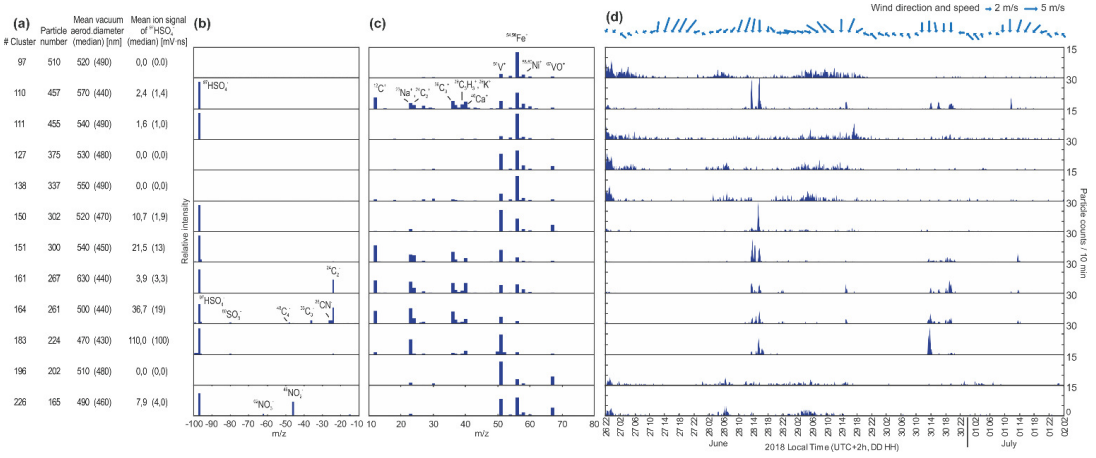

Figure 4: Results of the ART-2a clustering for 12 of the 15 clusters showing signatures of residual fuel combustion. (a) Cluster number according to their labels in the full cluster analysis (see Supplement), particle number, vacuum aerodynamic diameter and average sulfate signal of the clusters. (b) Weight matrices of negative ions and (c) positive ions corresponding to average mass spectra. (d) top: measured wind data; below: time series of particle counts with 10 min resolution. Note the different y-axis scales. While only mass spectral data was considered in the clustering algorithm, also the time series of the resulting clusters reveal two distinct groups: The transient group with bipolar mass spectra and short events as well as the background group with dominant metal signatures and smooth time series.

3.3.2 Mass spectral signatures for ageing of V-Fe-Ni particles

The main difference between the mass spectral signatures of the background group and the transient group is the limited number of negative ion signals and the weaker positive signatures from EC, OC, Ca^+ and Na^+ for the background particles. The absence of negative ion signals was often reported for SPMS studies on ambient air and is associated with water uptake during aerosol ageing (Moffet et al., 2008; Ault et al., 2010). Particles can acquire low- and semi-volatile material, e.g. ammonium sulfate or nitrate and organic species by condensation, coagulation or heterogeneous reactions (Seinfeld and Pandis, 2016). The increasing hygroscopicity and water uptake predominantly affects the formation of negative ions (Neubauer et al., 1998), but also suppression effects on positive ions were documented (Neubauer et al., 1997; Dall'Osto et al., 2006). Hatch et al. found that laser absorption and particle ablation in LDI are reduced from coatings of secondary species, finally affecting mass spectra for both polarities (Hatch et al., 2014). Also charge-transfer reactions in the plume play an important role, because they favour cations with low ionization potential and anions with high electron affinity (Reinard and Johnston, 2008). As an example, K^+ dominates the positive spectrum of wood combustion particles, see e.g. Fig. 2.

Previous studies have discussed the lack of negative ion mass spectra (Ault et al., 2009) and the balance between sulfate and nitrate (Liu et al., 2017) as indicators for atmospheric ageing of ship emission particles. However, a suppression of positive ions through ageing was not reported in these studies, although the mass spectra of substantially aged ship particles shown by Ault et al. (Ault et al., 2009) also reveal a low relative intensity of EC, OC, Ca^+ and Na^+ compared to the freshly emitted

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particles documented by in-port/near-port studies (Healy et al., 2009; Ault et al., 2010; Liu et al., 2017; Xiao et al., 2018). Generally, the formation of negative ions by electron capture requires previous generation of positive ions, and is therefore more prone to suppression effects than positive ion generation. In consequence, the relative heights of positive ion peaks apart from the transition metals may provide a further estimate for the amount of secondary species, water uptake and atmospheric ageing of ship particles. The respective mass spectral indicators for ageing of V-Fe-Ni particles are summarized in Table 1.

Table 1: Mass spectral signatures that indicate the degree of ageing for particles from residual fuel combustion.

	Neg. ion mass spectra	Pos. ion mass spectra	References
freshly emitted	EC, high-sulfur fuels: $^{-80}SO_3^-$, dominant $^{-97}HSO_4^-$	V-Fe-Ni, EC, OC, Na, Ca	(Ault et al., 2010; Healy et al., 2009; Xiao et al., 2018; Liu et al., 2017)
moderately aged, local – regional	$^{-97}HSO_4^-$	V-Fe-Ni, smaller EC, OC, Na, Ca	(Liu et al., 2017; Arndt et al., 2017; Gaston et al., 2013), this work
substantially aged, regional – long range	no signals or secondary sulfate, nitrate, methanesulfonate	dominant V-Fe-Ni	(Ault et al., 2009; Furutani et al., 2011; Arndt et al., 2017), this work

3.3.3 Metal signatures of V-Fe-Ni particles

In contrast to negative ions and EC, OC as well as alkali cations, the transition metal signals appear to be more stable and remain also after long-range transport (Furutani et al., 2011; Ault et al., 2009). Although only speculative here, sulfate-driven metals dissolution in the particle coating might be of importance (Fang et al., 2017). A difference to all previous SPMS studies on ship emissions is the strong Fe^+ signal, comparable to the V^+ peak and the remarkably Ni^+ signal in most particles. This can be attributed to the resonant ionization of Fe at 248 nm (Passig et al., 2020). Because of the increased signals for Fe (and possibly Ni) it appears feasible to evaluate whether V/Fe signal ratios may be indicative for a specific source, e.g. as a result of different fuel composition (Viana et al., 2009). However, from Fig. 4(c) and (d), it becomes apparent that the same transient events, respective sources, contribute particle clusters with very different V/Fe ratios. In general, background particles tend to show larger Fe and lower V signals compared to the transient group, but due to a number of exceptions (clusters 110 and 196) we cannot draw clear conclusions here. Note that the LDI signal strength in SPMS does not necessarily indicate the component's mass concentration. Beyond the transition metals, Ca^+ signals appear in all clusters of the transient group. Strong calcium signals from lubrication oil additives were frequently observed in SPMS studies on diesel engines (Toner et al., 2008; Shields et al., 2007), mainly because of its low ionization potential and high detection efficiency; and calcium was also found in particulate emissions from ships using residual fuels (Moldanová et al., 2009; Streibel et al., 2017).

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3.3.4 Sulfate signals

As apparent from the 4th row in Fig. 4(a) there are considerable differences in sulfate signals between the clusters of the transient group, with highest values for cluster 183. Although sulfate can also be secondary, freshly emitted plumes from sulfur-rich fuel combustion have particular high sulfate contents from gas-particle conversion of SO_2 (Murphy et al., 2009; Ault et al., 2010; Healy et al., 2009). With this regard, the temporal trend of the sulfate ion yield from all particles is plotted in Fig. 5(b) (yellow area), while the time series of all V/Fe/Ni-particles from Fig. 3(e) is again shown in Fig. 5(a) for comparison. The sulfate yield shows slightly elevated background for marine air during northern winds and some smaller features that are not correlated with the number of V-Fe-Ni particles. However, for some of the transients from V-Fe-Ni particles, we also find coinciding features of sulfate levels within the full particle ensemble. Comparison with the sulfate ion yield from only V-Fe-Ni particles (brown) reveals that this particle type contributes the main fraction of sulfate during these incidents.

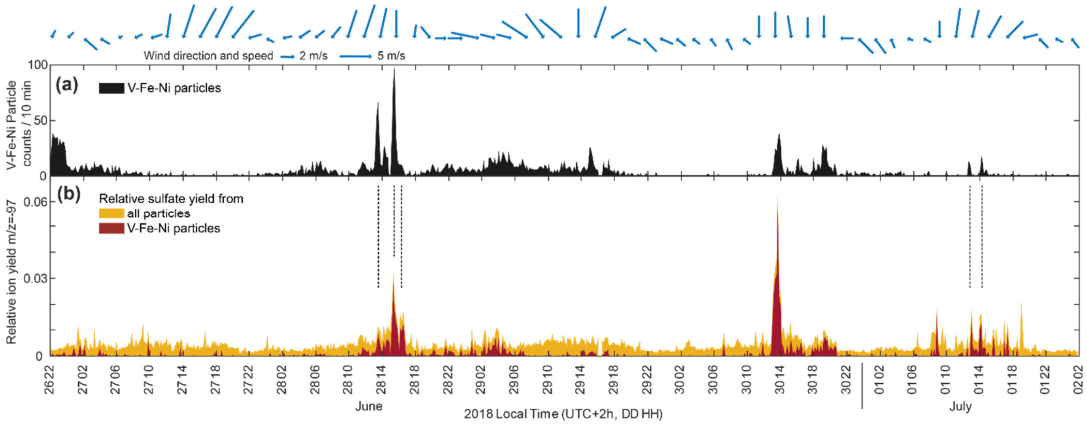

Figure 5: (a) Time series of V-Fe-Ni particles (same as Fig. 3e). (b) Yellow area: The ion yield of HSO_4^- normalized to the particle number per 10 minutes reveals coinciding sulfate events for some of the V-Fe-Ni features. The majority of sulfate is detected on the V-Fe-Ni particles itself (brown area). Most of these particles belong to cluster 183 in Fig. 4.

3.4 Assignment to ships

Land-based sources can be excluded for the transient group particles, because there are no refineries or chemical industry plants in the town and the local coal power plant was not in operation during measurements. There are two possible source regions of V-Fe-Ni particles: The main shipping lane (Kadet Channel, >50,000 passages per year), about 40 km north of the sampling site and the harbor of Rostock (≈7000 approaches, 75% ferries and roll-on-roll-off ships), located about 10 km north of the site, see Fig. 6(a). The complete Baltic Sea is a SECA, with a 0.1% limit for sulfur in fuel mass. Several studies assessed the compliance of ships to more than 95% (International Transport Forum Policy Papers, 2016; Lähteenmäki-Uutela et al., 2019), thus it is not very likely to detect many ship plumes from operation with conventional high-sulfur bunker fuel within

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the timeframe of about 36h with northern wind in our study. However, an increasing number of ships is currently equipped with scrubbers (Winnes et al., 2018), efficiently removing SO_2 from the exhaust with moderate effects on the PM emissions (Fridell and Salo, 2016; Lehtoranta et al., 2019). Several ships with scrubbers are known to regularly approach the port of Rostock. The ferry route to Denmark is operated with a pair of hybrid ferries (ferry A and B). These ships are equipped with scrubbers and use batteries for in-port manoeuvring. The diesel engines are started at the harbor exit, when entering open water, directly east of the meteorological station and 12 km north of the measurement site, see the enlarged view in Fig 6(a). On the way back, the engines are stopped at the same position. The typical turnaround time between two departures is 2h and 15 min, matching the delay between two major transient events during afternoon at the 28 June and 30 June, see Fig. 4(d).

We analyzed the AIS data to determine the departures and approaches of the ferries within the periods of northern wind. For the respective period at June 28, the times when the ferries pass the harbor exit, where the engines are typically started and stopped, are indicated in Fig 6(b). The time series of particles from the transient group reveal that the strong particle events follow these times with a delay of 45-60 min, in agreement with the wind speed of about 4 m/s. There was a further ferry 'C' with scrubber (no hybrid), approaching Rostock around 12:45 and leaving the port at 14:30 whose signals interfere with ferries A and B. For earlier and later departures and arrivals, the wind direction was unfavourable at this day.

Of note, the wind was initially analyzed using the HYSPLIT back trajectories, as shown by the red and blue lines in Fig. 6(a). From the blue trajectories, ending 15:00 local time at the measurement site, it appears unlikely that the V-Fe-Ni particle transients stem from the harbor area, as they indicate distant source regions along the main shipping route. However, there is substantial difference in wind direction between the trajectories and the wind data measured at the harbor exit, see blue arrows in Fig. 6. Using the measured wind data, the group of transient particle events at 28 June are in agreement with AIS data from the ferries, as previously discussed.

On the next day (29 June), there is no transient feature of comparable intensity. The wind turned rapidly from North-West to North-East, and air transport from the harbor to the site was only possible for a short period. However, a broader event, lasting about one hour around 15:00 can be noticed for particles of cluster 111 (Fig. 4). This cluster shows a different chemical profile, with solely sulfate in negative mode and marginal signals of EC, OC and alkali metals in positive mode, indicating substantial ageing and a more distant source, see section 3.3.2. Both the back trajectories as well as the measured wind data shown in Fig. 6(c) reveal a north-eastern direction, guiding air masses from the eastern Kadet channel to the site. Among six cargo ships, ferry C passed this stretch between 12:30 and 14:00 on its way from a different harbor to Sweden. This ferry is also equipped with a scrubber and therefore legally operated with heavy fuel oil, contributing a possible source for the detected V-Fe-Ni particles. Its position at 13:00 is indicated in Fig. 6(c), while the hybrid ferries A and B were in the harbor (engines off) in the relevant time between 14:00 and 15.00 and can therefore be excluded as source for the event. It appears likely that the event of cluster 111 at 29 June 15:00 results from regional transport from the Kadet channel. In conjunction with the strong transient signals from the 28 June, this suggests that long-range detection of residual fuel operation might be possible if the wind field is captured correctly and if the traffic is not too dense.

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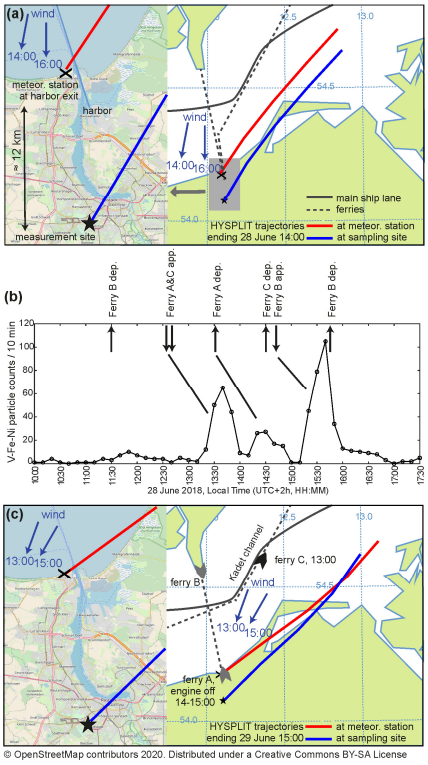

Figure 6: Assignment of transient particle events to distant ship passages. (a) For the first transients, observed on 28 June during a period of northern wind, the HYSPLIT trajectories indicate transport of particles from distant sea areas to the sampling site (star). However, the measured wind directions (blue arrows) in conjunction with ship transponder data reveal ferries with scrubbers as the probable source. (b) Time series of particles from the transient group during northern winds at June 28. The particle events follow the approach and departure times of the ferries (arrows) with a delay of about 45 min during optimum wind directions. (c) On 29 June, the wind direction is north-northeast and only one weak transient event appears (see Fig. 4). However, a broader feature of aged V-Fe-Ni particles at 15:00 indicate a distant source and ferry C is underway in the Kadet channel in the respective timeframe (and six further ships). The difference between trajectories and measured wind data emphasize the importance of accurate meteorological data in potential future monitoring systems.

At 30 June, there was a period of straight north winds and Fig. 4(d) shows several transient V-Fe-Ni particle events for this time, including a small dual peak pattern for cluster 110 with 2 h 15 min delay, matching to AIS-derived departures of ferry A and B, respectively. The time series of sulfate ion signals in Fig. 5(b) reveals a strong increase in sulfate levels that is mainly contributed by particles from cluster 183, compare Fig. 4. The event coincides with the aforementioned event from departure of ferry A and may be associated with scrubber malfunction or delayed onset of its operation. High sulfate emissions from ships that have installed scrubbers have previously been reported (Mellqvist et al., 2017b; Mellqvist et al., 2017a). However, a different source for the sulfate event, such as a further passing ship, cannot be excluded.

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The origin of the background particles with V-Fe-Ni signals cannot be attributed to individual ships. They may be associated with general ship traffic, which is also supported by their increase during wind from the western Baltic Sea and the North Sea. The high levels at beginning of the measurements followed a period of air mass stagnation in the western Baltic Sea, where emissions have probably been enriched and were then transported to the site by light winds. Ships can emit V-Fe-Ni particles under operation with residual fuels by using scrubbers or if non-compliant fuels or desulfurized hybrid fuels are used. However, Antturi et al. estimated in 2016, that only 136 of about 5000 ships sailing in the Baltic Sea had installed a scrubber and the large majority of ships use distillate fuels such as MGO (Antturi et al., 2016). Although scrubbers gain importance, a further source is conceivable: As shown in Fig. 4, all particle clusters that belong to the transient group show calcium signals from lubrication oil. While the size distribution of freshly emitted soot particles from diesel engines peaks well below 100 nm (Streibel et al., 2017; Oeder et al., 2015), the majority of particles in the accumulation modes show signatures of lubrication oil (Lyyränen et al., 1999; Sakurai et al., 2003; Toner et al., 2006). Because many ships run on residual fuels outside the SECAs and switch to low-sulfur distillate fuels when entering them (Van Roy, W and Scheldeman, K., 2016; Lähteenmäki-Uutela et al., 2019), their lubrication oil can contain metals from previous residual fuel operation that can consequently be emitted in small amounts also during operation in SECAs. Recently, also Zanatta et al. found a limited number of V-Fe particles in the marine boundary layer along ship lanes in the Baltic Sea using an aircraft-based SPMS (Zanatta et al., 2020).

Our analysis of AIS data revealed that a total number of 470 cargo ships, tankers and passenger ships of all sizes were sailing the major ship lane during our measurement period. It should be noted, that the ships running on distillate fuels such as MGO, cannot be separated from other fuel combustion sources by our approach. Considering the typical compliance rate and the small number of ships with scrubbers, it can be estimated that less than 10% of the particles from ships are V-Fe-Ni particles and therefore identified by our approach. Consequently, a substantial fraction of the EC-OC particles may also stem from ships, which is supported by the increased number of EC-OC particles during on-shore winds, see Fig. 3.

4. Conclusions

With the present study, we demonstrated the chemical detection of individual ship plumes from more than 10 km distance. It could be shown that also ships with installed scrubbers can be detected by their PM emissions indicating that the emissions of toxic transition metals from residual fuel combustion are not sufficiently abated by scrubbers. This emphasizes the need for additional cleaning technologies and cleaner fuels. By using chemical instead of physical indicators for the presence of ship plumes, we extended the approach of Ausmeel et al. to perform stationary measurements at some distance downwind of shipping lanes (Ausmeel et al., 2019). Of note, this change to chemical indicators renders the method independent from background aerosols, as long as source-specific and detectable markers exist. We analyzed mass spectral signatures for ageing of particles from residual fuel combustion and recommend to consider the suppression of positive ions apart from transition metals as additional ageing indicator for this particle class. The results furthermore suggest that the signal ratio between transition metals is not a suitable marker for individual ship assignment with SPMS.

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From analysis of transient particle events, wind data and ship transponder signals, it becomes apparent that accuracy in wind data, possible mixing of different plumes during high traffic and prevailing wind directions are key limiting factors rather than chemical detection limits or background air pollution. Consequently, SPMS-based monitoring systems should acquire local wind data and small-scale plume dispersion models should be integrated (Matthias et al., 2018; Badeke et al., 2020). The possible operation time is mainly limited by the prevailing wind directions, which should be perpendicular to the ship lane to avoid plume mixing and straight to the monitoring site. However, this limitation can be overcome by installation of multiple monitoring stations. Favorable places are opposite sides of straits, islands near major shipping routes and waterways to large ports. Mobile ship-based units could complement such monitoring networks.

While our approach can detect ships plumes from residual fuel operation, it is not applicable for monitoring of ship emissions from distillate fuels, because in its present form, it is not unambiguously separating ships running on MGO from land-based traffic emissions. Novel markers for ship emissions beyond the metal signatures have been identified, including source-specific signatures of polycyclic aromatic hydrocarbons (PAH) (Czech et al., 2017a; Czech et al., 2017b). Recent developments in SPMS allow to acquire detailed PAH-profiles from individual particles (Passig et al., 2017; Schade et al., 2019) and therefore they open a perspective towards a comprehensive monitoring protocol for ship emissions and individual plumes.

Data availability. Data are available on request from Johannes Passig (johannes.passig@uni-rostock.de).

Supplement. The supplement related to this article is available online at:

Author contributions. JP designed the experiments, analyzed data, prepared the figures and wrote the manuscript with contributions from all authors. JS and RI developed software and performed the experiments. LL, XL and ZZ provided the SPMS instrument. TA and RZ assisted with technical support, data interpretation and manuscript writing.

Competing interests. The authors declare that they have no conflict of interest.

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