

1 **Ship aerosol emissions and marine fuel regulations:**
2 **Impacts on physicochemical properties, cloud activity**
3 **and emission factors**

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12 **Key Points:**

- 13 • Low sulfur content fuels can reduce emissions of ultrafine particulate matter sig-
14 nificantly.
- 15 • Exhaust wet scrubbing shifts particle size distributions and reduces soot emissions.
- 16 • Usage of low sulfur content fuels or exhaust wet scrubbing have opposing effects
17 on CCN activity of ship exhaust particles.

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Abstract

Marine regulations aim to reduce sulfur and nitrogen exhaust emissions from maritime shipping. Here, two compliance pathways for reducing sulfur dioxide emissions, fuel sulfur content reduction and exhaust wet scrubbing, are studied for their effects on physicochemical properties and cloud forming abilities of engine exhaust particles. A test-bed diesel engine was utilized to study fresh exhaust emissions from combustion of non-compliant, high sulfur content fuel with (WS) and without (HiS) the usage of a wet scrubber as well as a regulatory compliant, low sulfur content fuel (LoS). Particle number emissions are decreased by $\approx 99\%$ when switching to LoS due to absence of 20-30 nm sulfate rich particles. While number emissions for WS are also decreased, a shift in the sulfate mode towards larger sizes was found to increase particle mass emission factors by at least 31%. Changes in the mixing state induced by the compliance measures are reflected in the hygroscopicity of the exhaust particles. Fuel sulfur reduction decreased cloud condensation nuclei emissions by at least 97% due to emissions of primarily hydrophobic soot particles. Wet scrubbing increased those emissions, mainly driven by changes in particle size distributions. Our results indicate that both compliance alternatives have no obvious impact on the ice forming abilities of 200 nm exhaust particles. These detailed results are relevant for atmospheric processes and might be useful input parameters for cloud-resolving models to investigate ship aerosol-cloud interactions and to quantify the impact of shipping on radiative budgets from local to global scales.

Plain Language Summary

We investigate how two pathways to comply with international regulations, aiming to reduce emissions of atmospheric pollutants from ships, alter properties of exhaust particles. Both investigated compliance measures (i.e. combustion of cleaner, low sulfur content fuels and aftertreatment of exhaust from a high sulfur content fuel via wet scrubbing) have substantial impacts on the chemical and physical properties of these particles. We find that, while both alternatives reduce the total number of emitted particles substantially, the effect on emissions of cloud forming particles is path dependent. While fuel sulfur content reduction decreased the number of cloud forming particles by about 97%, wet scrubbing led to a strong increase in emissions, suggesting that the measures can have substantial and opposing impacts on local cloud formation and evolution.

1 Introduction

Maritime shipping is a major source of greenhouse gases, such as carbon dioxide, CO₂, and atmospheric pollutants, including nitrous oxides, NO_x, sulfur dioxide, SO₂, and exhaust particles in the form of soot and sulfate that can have negative impacts on human health and ecosystems. Exhaust particles from ships have been found to impact human health along coasts and in areas close to major shipping lanes due to high ultra-fine particle numbers and the chemical compositions of these particles (Corbett et al., 2007; Liu et al., 2016). Ship exhaust particles generally consist of carbonaceous matter, often in the form of soot or other organics, inorganic species, such as sulfate, ash and can also contain different metals minerals originating from the fuels or lubricating oils (Popovicheva et al., 2009; Moldanová et al., 2013; Eichler et al., 2017). Given the range of fuel types and engines used in the shipping sector, the relative contributions between constituents can vary significantly.

To address air pollution from ship exhaust particles the International Maritime Organization (IMO) has been implementing international regulations, which target emission reductions of sulfur oxides (SO_x) and also, indirectly particulate matter from ships. The regulations mandate ship owners emit less SO₂. Operators can achieve this by transitioning to higher grade marine fuels with lower fuel sulfur content (FSC) or by installing

67 exhaust abatement systems, such as wet scrubbers, which are primarily designed to re-
68 move SO_2 from the exhaust. In the absence of SO_2 removal systems, the FSC of marine
69 fuels is limited to 0.5% by mass (hereafter abbreviated by %). In sulfur emission con-
70 trol areas (SECA), which include the Baltic and North Sea area among others, regula-
71 tions are stricter and the FSC of marine fuels may not exceed 0.1% (IMO, 2008).

72 Recent studies show that particulate emissions have coincidentally been reduced
73 following the implementation of both, a 2015 0.1% SECA limit and a global 2020 0.5%
74 FSC cap (Anastasopoulos et al., 2021; Seppälä et al., 2021; Yu et al., 2020, 2023; Wu et
75 al., 2020). This complimentary particle reduction is likely caused by shifts towards higher
76 grade residual fuel oils and distillate fuels or due to blending of fuels to meet FSC com-
77 pliance levels. Anastasopoulos et al. (2021), for example, investigated effects after imple-
78 mentation of the aforementioned restrictions on particulate matter emissions along coastal
79 areas in North America and observed large reductions in SO_2 and particulate matter con-
80 centrations (up to 83% and 37% respectively). Moreover, a ship plume intercept study
81 over the Baltic Sea found ambient particle concentrations to be reduced by up to 32%
82 after implementation of the 0.1% SECA FSC restrictions (Seppälä et al., 2021). Sim-
83 ilar reductions of particulate matter emissions were also observed for ships utilizing fu-
84 els with FSCs below 0.5% (Yu et al., 2020, 2023). While one study showed that ships
85 at berth emitted on average 56% less particles, restrictions were also found to affect the
86 emission characteristics of volatile organic compounds and the potential for secondary
87 aerosol and ozone formation to be significantly increased which has implications for lo-
88 cal air quality (Wu et al., 2020). Despite implementations of stricter FSC restrictions
89 and a resulting reduction in emission of various air pollutants, ship related emissions of
90 particulate matter and NO_x can still be a major burden on ambient air quality in ma-
91 jor port areas (Zhai et al., 2023). While a clear trend for particle number concentration
92 reductions is seen, transitions towards lower FSC fuels have also been found to reduce
93 the potential of exhaust particles to form liquid droplets at atmospherically relevant su-
94 persaturations. This decrease of cloud condensation nuclei (CCN) emissions is due to
95 reduced emissions of more hygroscopic particles and shifts towards emissions of gener-
96 ally smaller particles, which have higher droplet activation thresholds (Yu et al., 2020,
97 2023; Santos et al., 2023).

98 While wet scrubbing has been found to reliably decrease ship exhaust SO_2 emis-
99 sions to IMO compliant levels, recent studies on exhaust particle removal efficiencies show
100 varying results. Fridell and Salo (2016) found particle number concentrations to be re-
101 duced by approximately 92% and Winnes et al. (2020) found significant reductions in
102 total number emissions but not in the solid fraction of exhaust particles. Conversely, other
103 studies report only minor reductions in total particle number concentrations (Lehtoranta
104 et al., 2019) or find only particles above $1 \mu\text{m}$ to be efficiently removed (Zhou et al., 2017).
105 Similarly, Yang et al. (2021) found particulate matter below $2.5 \mu\text{m}$ to be reduced by
106 $\approx 10\%$ but found the level of sulfate particles to be hardly affected. More recent wet scrub-
107 ber studies investigated the implementation of a wet electrostatic precipitator (WESP)
108 after a scrubber and found that up to 98% of the exhaust particles were removed (Jeong
109 et al., 2023; Järvinen et al., 2023). Moreover, exhaust particle wet scrubbing has been
110 found to affect the composition and mixing state of exhaust particles (Lieke et al., 2013;
111 Santos et al., 2023), which can alter their roles in atmospheric processes, for example,
112 by facilitating liquid droplet formation (Santos et al., 2023). The introduction of exhaust
113 wet scrubbing in the shipping sector has also gained attention for its potential hazardous
114 impacts on the marine environment and its lifeforms. Studies have found that open-loop
115 scrubbing leads to concentrated emissions of metals and PAHs to the water and can also
116 lead to emissions of new contaminants, like chromium (Lunde Hermansson et al., 2021;
117 Ytreberg et al., 2022).

118 Maritime shipping emissions and ship track observations provide a good opportu-
119 nity to study the role of anthropogenic emissions on the climate system. For instance,

120 the recent introduction of the global 0.5% FSC limit can be used to investigate the im-
121 pact of reduced SO_x emissions from ships on cloud formation and properties, and to bet-
122 ter quantify radiative forcing. Yuan et al. (2022) found that the 2020 FSC cap led to a
123 decrease in ship track frequency and subsequently a reduction of climate cooling from
124 emitted aerosol particles. While Gryspeerdt et al. (2019) observed large reductions in
125 ship track numbers between 2014 and 2015 and highlight sulfate as the key component
126 in ship track formation, they also point out difficulties in detecting ship tracks due to
127 uncertainties in background cloud states, which can lead to an underestimate of the ac-
128 tual impact from shipping. Similarly, Manshausen et al. (2022) found that ships can form
129 “invisible” tracks, which may not be directly visible but their aerosol emissions can still
130 alter cloud properties. These uncertainties in quantifying climate impacts from maritime
131 shipping have also been highlighted by Watson-Parris et al. (2022), which found that an
132 80% reduction in SO_x emissions only accounted for a 25% decline in ship-track frequency.
133 Moreover, Diamond (2023) found changes in large-scale cloud properties and a decrease
134 in cloud brightening, results in a positive radiative forcing in a major shipping corridor.
135 Thus, the impact of new fuels and their potential to influence future climate means it
136 is important to improve our understanding of ship aerosol, cloud and climate interac-
137 tions.

138 In this study a diesel test-bed engine was used to characterize how international
139 regulations targeting emission reductions of airborne pollutants from the shipping sec-
140 tor, i.e. usage of low FSC fuels and wet scrubbers, alter physicochemical properties of
141 submicron exhaust particles and their abilities to act as cloud forming particles. Mea-
142 surements of particle size distributions, effective densities and chemical mixing states of
143 exhaust particles allow us to explain observed changes in CCN activation behavior. More-
144 over, this study investigated how both compliance measures as well as variations in en-
145 gine load affect particle number and mass emissions of submicron exhaust particles and
146 CCN and INP emissions at atmospherically relevant supersaturations.

147 2 Methods

148 2.1 Overview

149 Engine experiments were conducted between May 12th and June 7th, 2022 to de-
150 termine how FSC reduction and exhaust wet scrubbing affect characteristics of partic-
151 ulate exhaust emissions. A range of gas and aerosol measurement instrumentation was
152 used during these experiments. An overview of the experimental setup is shown in Fig-
153 ure 1, and the following sections discuss individual components in more detail. The re-
154 sults presented in this study reflect stabilized combustion conditions. During operations
155 that affected combustion conditions and exhaust emissions, such as the switching of fu-
156 els or engine loads, the gas and PM data was closely observed until it stabilized, which
157 could take between 5 and 20 minutes depending on the operation.

158 2.2 Engine, Fuels and Laboratory Wet-Scrubber

159 Engine experiments were performed at Chalmers University of Technology in Swe-
160 den using a Volvo D13K540 Euro 6 common rail, four-stroke diesel engine equipped with
161 six cylinders, a bore of 131 mm and a stroke of 158 mm. The engine’s on-road aftertreat-
162 ment system was removed prior to experiments. The engine was operated at 1200 rpm
163 during experiments, resulting in a maximum torque of 2600 Nm and maximum power
164 output of 349 kW. To study the engine load dependence of particle exhaust emissions,
165 measurements were performed at engine load points of 25% (≈ 85 kW), 50% (≈ 168
166 kW) and 70% (≈ 245 kW). The tested engine loads were determined from the ratios be-
167 tween measured and maximum torque at 1200 rpm.

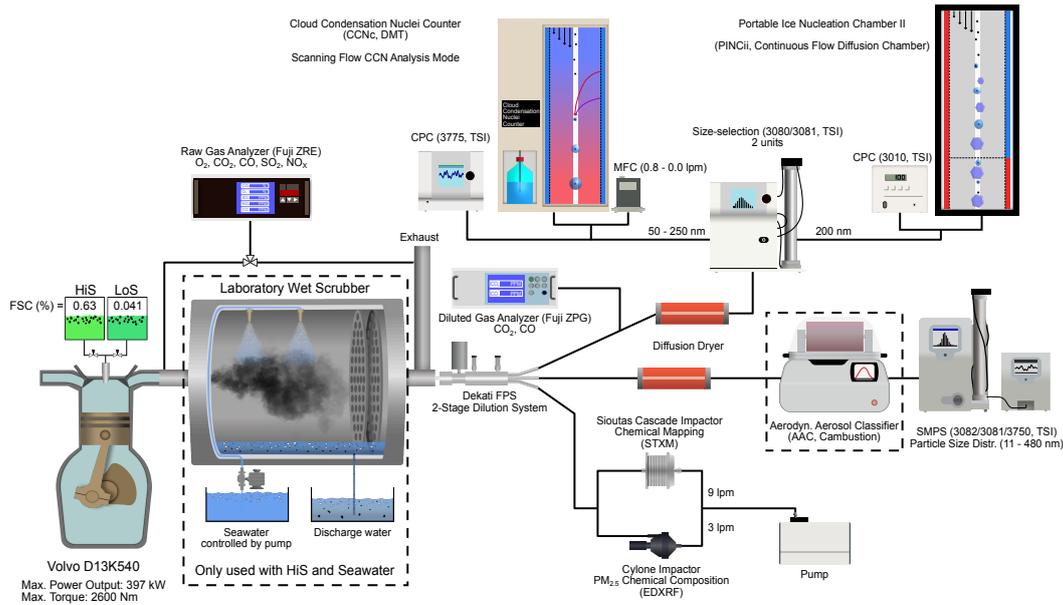


Figure 1. Schematic of the experimental setup. Sample aerosol is generated from a Volvo D13K540 engine using a non-compliant high sulfur content fuel (HiS; FSC = 0.63%), SECA compliant marine gas oil with a sulfur content fuel of 0.041% (LoS) and HiS fuel in combination with a laboratory wet scrubber. During wet scrubber experiments, a valve system was used to divert a portion of the total exhaust flow through the scrubber unit. Dashed boxes signify systems that could be bypassed.

168 To investigate the effects of FSC on physicochemical properties and cloud activ-
 169 ity of exhaust particles, two fuels were used during the experiments. Here, the baseline
 170 case (no compliance) is a marine distillate fuel with a FSC of 0.86% (HiS) exceeding the
 171 global FSC limit of 0.5%. Note that HiS fuel is a distillate fuel and thus, has a lower den-
 172 sity and viscosity compared to residual fuel oils, which are also commonly used in mar-
 173 itime shipping. The compliant, low FSC fuel used during experiments was marine gas
 174 oil (MGO) which had a FSC of 0.041% and is commonly used in the shipping sector. This
 175 case will be referred to as LoS. Fuel characteristics details are found in Table 1.

176 A custom-built, laboratory-scale wet-scrubber engineered at Chalmers University
 177 of Technology was used during specified experiments to reduce SO_x emissions from HiS
 178 combustion and to study the effects of wet scrubbing on exhaust particles. The unit con-
 179 sists of a horizontal, cylindrical 50 cm arranged stainless steel tank with an inner diam-
 180 eter of 40 cm. In total, seven nozzles, controlled by a pressure pump, are used to spray
 181 a fine mist of seawater into the exhaust gas. Three perforated demister plates are mounted
 182 inside the scrubber to enhance droplet removal from the exhaust gas before it leaves through
 183 the outlet. A more detailed description of the wet-scrubber can be found in Santos et
 184 al. (2022). In addition, lattice-structured packing material was placed between the demis-
 185 ter plates to increase surface interaction between exhaust gas and packing material to
 186 enhance the particle and droplet removal efficiency. Seawater used during the experiments
 187 was obtained from University of Gothenburg's Kristineberg Center for Marine Research
 188 and Innovation located on the Gullmar fjord in western Sweden ($58^\circ 14' 59.7'' \text{N}$ $11^\circ 26' 41.3'' \text{E}$).
 189 The facility possesses a seawater system with an intake depth of 32 m.

Table 1. Fuel properties. The cetane numbers for the tested fuels were within specifications for the engine. Fuel analysis was conducted by Saybolt Sweden in Gothenburg.

	HiS	LoS
Density at 15°C (kg/m ³)	865.7	837.3
Heat of Combustion (MJ/kg)		
Gross Heat of Combustion	45.10	45.73
Sulfur content (mass %)	0.63	0.041
Aromatic content (mass %)		
Total aromatics	32.5	22.3
Mono-aromatics	20.8	18.3
Di-aromatics	10.2	3.5
Tri+aromatics	1.5	0.5
Additive and Wear Metals (mg/kg)		
B	0.17	<0.1
K	0.29	0.60
Al, Ca, Cr, Cu, Fe, Pb	<0.1	<0.1
Ni, Na, V, P, Sn, Zn, Zi	<0.1	<0.1

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2.3 Gas and Aerosol Instrumentation

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Raw exhaust gas was diluted using a 2-stage dilution system (FPS-4000, Dekati Ltd., Finland) consisting of a temperature-controlled porous tube diluter as the first stage and an ejector diluter as the second stage. A single-beam NDIR analyzer (Model ZRE, Fuji Electric Co., Ltd., Japan) was used to measure relevant gaseous compounds including O₂, CO₂, CO, NO_x and SO₂ in the raw exhaust. The CO₂ concentration after the dilution system was measured with a Fuji ZPG CO and CO₂ analyzer (Fuji Electric Co., Ltd., Japan) and corrected for background CO₂ concentrations measured before engine start up. The ratios between CO₂ concentrations in the raw and diluted exhaust gas were used to calculate dilution ratios. A dilution system was used because high particle concentrations in the raw exhaust gas would have saturated most of the aerosol measurement instrumentation.

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The diluted sample aerosol was dried using silica gel diffusion dryers before being passed to the particle analysis instrumentation. Particle size distributions (PSD) were measured using a scanning mobility particle sizer (SMPS; Electrostatic classifier, EC, Model 3080L, and condensation particle counter, CPC, Model 3075, TSI Inc., USA). The SMPS was operated with a sample flow of 0.5 l min⁻¹ and a sheath flow of 5 l min⁻¹ and measured mobility diameters (d_{mo}) from of 11 nm to 470 nm. All PSDs were corrected for dilution factors as well as diffusional losses within the sampling lines following methodology outlined in Hinds (1999).

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2.4 Effective Density Measurements and Calculations

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Combined measurements of particles' aerodynamic diameters (d_{ae}) and their corresponding d_{mo} enable determination of the corresponding particle masses (m) as described by Tavakoli and Olfert (2014),

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$$m = \frac{\pi\rho_0}{6} \frac{C_c(d_{ae})d_{ae}^2d_{mo}}{C_c(d_{mo})}, \quad (1)$$

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where ρ_0 is 1000 kg m⁻³ and C_c is the Cunningham slip correction factor. To perform particle mass measurements, an Aerodynamic Aerosol Classifier (AAC, Cambustion Ltd.,

UK), which could be bypassed, was installed upstream of the SMPS measuring PSDs. The AAC was used to size-select particles from the polydisperse sample aerosol by aerodynamic diameter in the range between 50 nm and 250 nm. Continuous downstream SMPS measurements resulted in size distributions which were used to derive the corresponding d_{mo} . This was achieved by Gaussian least-squares fitting of the output data. In instances where multiple particle modes were observed in the SMPS data, which can suggest the presence of particles with different morphologies and compositions, multimodal Gaussian fits were applied. These modes were categorized into different particle types which are associated with particle modes in measured size distributions.

The effective density (ρ_{eff}) of a particle is defined as its mass divided by the volume of a sphere with a diameter equal to the particle's mobility diameter. Using this definition and combining it with Equation 1, it follows that,

$$\rho_{\text{eff}} = \frac{6m}{\pi d_{\text{mo}}^3} = \rho_0 \frac{C_c(d_{\text{ae}})d_{\text{ae}}^2}{C_c(d_{\text{mo}})d_{\text{mo}}^2}. \quad (2)$$

2.5 Energy Dispersive X-ray Fluorescence (EDXRF)

Trace element concentrations from PM_{2.5} (particulate matter $\leq 2.5 \mu\text{m}$) collected on filters were measured using energy dispersive X-ray fluorescence (EDXRF) spectrometry. Samples were collected on 25 mm diameter NucleporeTM track-etched membranes with a pore size of $0.4 \mu\text{m}$ (Whatman[®]) using a cyclone impactor with a 50% efficiency cut-off diameter of $2.5 \mu\text{m}$. Sampling times varied between 25 and 75 minutes. EDXRF measurements were performed using a SPECTRO XEPOS analyzer (SPECTRO Analytical Instruments GmbH, Germany) controlled by the XRF Analyzer Pro software (AMETEK, USA). Each filter was analyzed at least three times. Moreover, all results were corrected for background values by analyzing blank filter membranes. Raw data output was converted into element-specific emission factors by taking into account the sampling times, dilution factors and the fuel consumption for each individual filter.

2.6 Scanning Transmission X-ray Microscopy (STXM) and Near-edge X-ray Absorption Fine Structure (NEXAFS)

More filter samples were collected for chemical mapping and X-ray microscopy imaging using a Sioutas five-stage cascade impactor and standard transmission electron microscopy (TEM) copper mesh grids (Ted Pella Inc.). All samples were collected on stages C and D at a flow rate of 9 l min^{-1} , resulting in a particle size range of 0.25 to $0.5 \mu\text{m}$ and $<0.25 \mu\text{m}$ respectively. These sampling times varied between 5 and 15 minutes.

Scanning transmission X-ray microscopy (STXM) coupled with near-edge X-ray absorption fine structure spectroscopy (NEXAFS) enables chemical analysis and morphological inspection of individual aerosol particles. The combined method results in detailed information of, for example, functional groups, particle mixing state and structure and morphology of sampled particles. In STXM-NEXAFS, the TEM grid samples are exposed to soft X-rays of adjustable energy inside a vacuum chamber. At energies close to the ionization threshold inner-shell electrons can absorb enough photons to be excited into unoccupied orbitals, which is referred to as absorption edge and is element specific (Moffet et al., 2010). These element- and energy-specific absorption edges help to identify the chemical composition(s) of samples, including the detection of specific functional groups. STXM measurements are conducted under high vacuum conditions, meaning there does exist the potential for volatile species to escape.

The STXM analysis was performed at the BL4U beamline at the UVSOR Synchrotron Facility in Okazaki, Japan and at the SoftiMAX beamline at MAX IV laboratory in Lund, Sweden. Both STXM beamlines cover energy ranges between 75 eV and 1 keV and 275 eV and 2.5 keV respectively, allowing measurements at the K-edges of carbon (280-300

265 eV), nitrogen (393-425 eV), oxygen (525-550 eV) and sodium (1068-1095 eV) as well as
 266 at the sulfur L-edge (159-196 eV).

267 Initial processing of data, such as image alignment, correction for background sig-
 268 nal and conversion of flux data to optical density, was done using AXIS 2000 (*Hitchcock*
 269 *Group Homepage*, n.d.).

270 **2.7 Cloud Condensation Nuclei Counter (CCNC) Measurements and** 271 **Calculations**

272 The CCN activity of size-selected exhaust particles was determined using a single
 273 column CCN counter (CCNC; CCN-100, DMT). The supersaturation (SS) inside the
 274 growth chamber of the CCNC can be varied by either adjusting the sample flow rate (Q)
 275 or the stream-wise temperature gradient (ΔT). Details of the working principal are de-
 276 scribed in Roberts and Nenes (2005) and Lance et al. (2006). Exhaust particles were size-
 277 selected using a DMA (Model 3080L, TSI Inc., USA) covering a d_{m0} range between 50
 278 nm and 250 nm. A CPC (Model 3775, TSI Inc., USA) measured the total particle num-
 279 ber concentrations (N_P) parallel to the CCNC to infer activated fractions (AF), that
 280 is the ratio between the number of activated particles and the total amount of particles.

281 During the engine experiments the CCNC was operated in Scanning Flow CCN Anal-
 282 ysis (SFCA) mode (Moore & Nenes, 2009). This method allows for continuous measure-
 283 ments of SS spectra by ramping the sample flow rate while keeping ΔT constant. The
 284 sample flow rate was increased from 0.2 to 1.0 l min⁻¹ at a constant rate for 120 s. At
 285 0.2 and 1.0 l min⁻¹ the sample flow was kept constant for 30 s. A mass flow controller
 286 (MFC) operated in parallel to the CCNC to maintain a total size-selected sample flow
 287 rate ($Q_{CCNC} + Q_{MFC}$) of 1.0 l min⁻¹. Supersaturation spectra were measured at $\Delta T =$
 288 4, 10 and 18°C, resulting in a SS range of about 0.07 - 2.4%. Individual CCN spectra
 289 were visually inspected and multiple charging artifacts were accounted for by identifi-
 290 cation of pre-activation plateaus. Critical supersaturations (SS_c ; activation of 50% of
 291 the size-selected singly charged particle population into cloud droplets) were determined
 292 by fitting the measured activation curves to sigmoidal functions following Moore and Nenes
 293 (2009),

$$294 \frac{N_{CCN}}{N_P} = a_0 + \frac{a_1 - a_0}{1 + (Q_{CCNC}/Q_{50})^{-a_2}}, \quad (3)$$

295 where a_0 , a_1 , a_2 and Q_{50} are the minimum, maximum, slope, and inflection point respec-
 296 tively. Data were converted from Q_{50} to SS_c using linear fits derived from instrument
 297 calibrations (see Supplemental Information; Figure S1). The CCNC was calibrated dur-
 298 ing the campaign using $(NH_4)_2SO_4$ particles generated from an aerosol generator (3079A,
 299 TSI Inc., USA).

300 The resulting SS_c values were converted to the dimensionless hygroscopicity pa-
 301 rameter (κ) using,

$$302 \kappa = \frac{4A^3}{27d_{m0}^3 \ln^2(1 + SS_c/100\%)}, \text{ with } A = \frac{4\sigma_w M_w}{RT\rho_w}, \quad (4)$$

303 where SS_c is given in %, $\sigma_w = 71.99$ mN m⁻¹ is the surface tension of water at 25°C,
 304 M_w is the molar mass of water, R is the universal gas constant, T is the absolute tem-
 305 perature and ρ_w is the density of water at 25°C ($\rho_w = 0.997$ g cm⁻³; Petters and Krei-
 306 denweis (2007)).

307 **2.8 Ice Nucleation Measurements with the Portable Ice Nucleation Cham-** 308 **ber II (PINCii)**

309 The Portable Ice Nucleation Chamber II (PINCii) is a newly developed continu-
 310 ous flow diffusion chamber (CFDC) built to investigate ice nucleation by aerosol parti-
 311 cles (Cestarède et al., 2023). During measurements with PINCii, RH ramps for three

312 to four pre-selected lamina temperatures were performed, i.e., during each ramping cycle
 313 both wall temperatures are continuously adjusted so that the temperature in the sam-
 314 ple flow lamina remains constant but the relative humidity with respect to ice (RH_i) is
 315 steadily increased. This method allows the temperature- and humidity-dependent ice nu-
 316 cleation onsets to be determined for aerosol particles over a wide range of conditions. Ramp-
 317 ing experiments were performed at -26°C , -34°C (WS only), -38°C , -42°C (WS only)
 318 and -50°C and covered a RH_i range of 110% to 160%. Size-resolved ice crystal concen-
 319 trations were obtained from an optical particle counter (OPC; Remote 3104, Lighthouse
 320 Worldwide Solutions, USA) at the PINCii outlet. The OPC has four size channels: (1)
 321 $0.3 \leq d_p < 1 \mu\text{m}$; (2) $1 \leq d_p < 3 \mu\text{m}$; (3) $3 \leq d_p < 5 \mu\text{m}$ and (4) $d_p > 5 \mu\text{m}$. Parti-
 322 cle counts for size channels 3 and 4, i.e. $d_p > 3 \mu\text{m}$, were considered as ice crystals in
 323 our results (Castarède et al., 2023). Between transitions to new lamina temperature set-
 324 tings, a solenoid valve at the inlet of PINCii switched to sample HEPA filtered ambient
 325 air for 15 minutes to measure background ice crystal concentrations and to correct val-
 326 ues obtained from ramping experiments. Before entering PINCii, particles in the sam-
 327 ple flow were dried using a diffusion dryer and size-selected using a DMA (Model 3080L,
 328 TSI, USA) to generate a monodisperse aerosol of $d_{\text{mo}} = 200 \text{ nm}$. Downstream of the
 329 DMA, the monodisperse sample flow was split and directed both towards PINCii and
 330 a CPC (Model 3010, TSI, USA), which was used to infer activated fractions, i.e. the ra-
 331 tio between measured ice crystals and the total particle concentration. Ice nucleation mea-
 332 surements were only performed during experiments with 50% engine load.

333 2.9 Calculation of Emission Factors

334 The amount of PN and PM emitted per kg of fuel burned were calculated as

$$\text{EF}_x = \frac{Q_{\text{exh}} C_x}{FC}, \quad (5)$$

335 where Q_{exh} is the exhaust gas flow in $\text{m}^3 \text{ h}^{-1}$, C_x is the number or mass concentration
 336 of a variable per m^3 , and FC is the load and fuel dependent fuel consumption in kg h^{-1} .
 337 To calculate particle number emission factors (EF_{PN}), particle size distributions were
 338 integrated and corrected for dilution factors and diffusional losses. Particle mass emis-
 339 sion factors (EF_{PM}) were derived by either assuming a particle density of 1 g per cm^3
 340 ($\text{EF}_{\text{PM},\rho_0}$) or by using mean effective density values for individual size distribution modes
 341 ($\text{EF}_{\text{PM},\rho_{\text{eff}}}$), to give more realistic estimates. We want to stress that EF_{PM} estimates are
 342 only valid for mobility diameters smaller than 500 nm and thus, lead to a potentially non-
 343 negligible underestimate as particles of larger sizes, which are few in numbers but tend
 344 to dominate particle mass distributions, are generally co-emitted from these types of com-
 345 bustion engines (Fridell et al., 2008; Popovicheva et al., 2009; Moldanová et al., 2009).

346 In order to estimate CCN emission factors normalized by particle number concen-
 347 trations and fuel consumption, a simple model approach as described by Kristensen et
 348 al. (2021) and Santos et al. (2023) is used. In this method, κ values for the entire size
 349 range of measured particle size distributions were derived by interpolating results ob-
 350 tained from CCNC measurements at distinct particle sizes. For particles smaller than
 351 50 nm and larger than 150 nm κ values were kept constant at the respective threshold
 352 values. Interpolated κ values were subsequently converted into critical supersaturations
 353 following Petters and Kreidenweis (2007), which allows activated fractions of CCN for
 354 individual size distributions at a given supersaturation to be calculated. Individual ac-
 355 tivated fractions are thereafter converted into CCN emission factors (EF_{CCN}) using,

$$\text{EF}_{\text{CCN}} = \frac{Q_{\text{exh}} N_{\text{CCN}}(SS)}{FC}, \quad (6)$$

357 where $N_{\text{CCN}}(SS)$ is the number concentration of CCN as a function of SS in $\# \text{ m}^{-3}$,
 358 Q_{exh} is the exhaust gas flow in $\text{m}^3 \text{ h}^{-1}$ and FC is the load and fuel dependent fuel con-
 359 sumption in kg h^{-1} .

3 Results and Discussion

3.1 Evaluation of Wet Scrubber SO₂ Removal Efficiency

Guidelines for exhaust gas cleaning systems outlined by the IMO mandate that ships utilizing exhaust wet scrubbers need to meet certain SO₂/CO₂ emission standards. If ships operate wet scrubbers outside of SECAs with fuels exceeding FSCs of 0.5%, the ratio between emitted SO₂ (in ppm) and CO₂ (in %) may not exceed a value of 21.7. In SECAs, where the maximum allowed FSC is limited to 0.1%, this ratio needs to be below 4.3 (IMO, 2021b).

During experiments performed at the 25% engine load point, the scrubber was able to reduce SO₂ to a ratio of at least 0.9 and consistently achieved SECA compliance levels. At 50% load, the ratio varied between 4.3 and 6.3, i.e., a reduction to a SECA compliance level was possibly not reached. Similarly, at the highest load point of 75%, the SO₂/CO₂ ratio was reduced to 8.2, meaning that for the SO₂ measurement periods post scrubber, only global compliance could be achieved.

Determination of the scrubber's SO₂ removal efficiency was limited by sampling issues associated with the SO₂ monitor when measuring downstream of the scrubber. The high humidity in the sample air caused the gas monitor's condenser to deteriorate, which caused the measuring cell's pump to shut down. As a result, sampling downstream was limited to brief time periods, meaning that the SO₂ signal was often not stabilized before pump failure. Therefore, measured reduction values represent the minimum SO₂ reduction.

Other laboratory parameters in this study serve to reinforce the idea that these measurements represent one outcome of a spectrum that would be possible in the open seas. It has also been shown that SO₂ uptake in seawater depends on its salinity and alkalinity. Waters from the Kattegat and Baltic Sea have typically lower values compared to open-ocean seawater, which means that that SO₂ removal efficiency would potentially increase if seawater of higher salinity and alkalinity was used (Karle & Turner, 2007). In general, all of these factors will be true of real ships operating in real oceans, where both the loose regulation and natural heterogeneity mean there is a wide envelope of operational conditions.

3.2 Particle Size Distributions

Particle number size distributions measured with the SMPS for different engine load conditions are shown in Figure 2. Data displayed in the figure are averages of measurement periods where corresponding shaded areas depict measured uncertainties as \pm one standard deviation. In order to derive statistical information on the data, weighted non-linear least-squares fits were applied (see Figures S5, S6 and S7). In some cases, fitting three modes to the size distributions reduced the residuals. Nevertheless, the discussion here is limited to uni- and/or bimodal modal fits.

The non-compliant HiS case shows at least one dominant mode between 18 and 25 nm and a second mode between 50 and 62 nm. Comparable size distributions have been measured, for example, by Kasper et al. (2007); Corbin et al. (2018) and Alanen et al. (2020) using a range of different engine and fuel types. In these cases, particles in the smaller mode probably originate from nucleation of volatile substances that are organic, inorganic or sulfurous in nature (Sippula et al., 2014). Particles in the larger mode often consist of mostly solid, fractal-like soot particles (Anderson et al., 2015; Corbin et al., 2018; Alanen et al., 2020).

When switching to the compliant LoS fuel, the measured size distributions changed significantly compared to HiS. The LoS size distributions are dominated by a single mode between 41 and 53 nm. Particles within this mode are most likely soot-type particles.

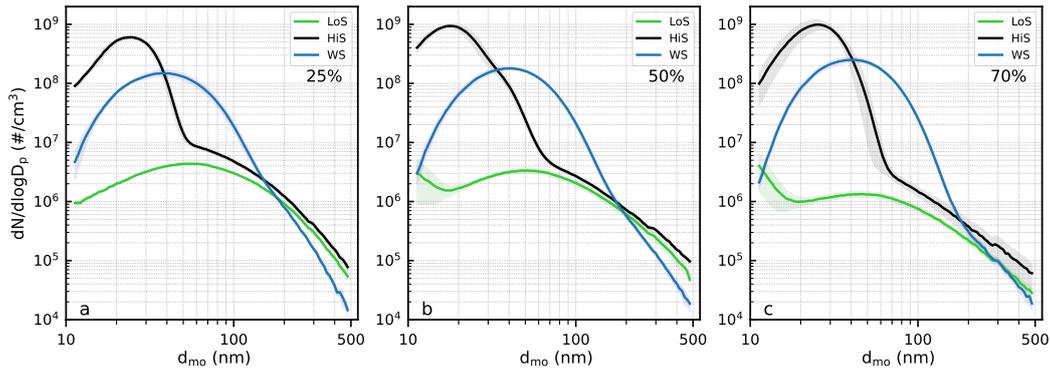


Figure 2. Average particle size distributions measured with the SMPS for the low FSC fuel (LoS), the high FSC fuel (HiS) and where HiS exhaust gas is passed through the wet scrubber using seawater (WS) are shown in panels (a) to (c). Respective panel show size distributions measured for 25%, 50% and 70% engine load regimes. The shaded areas depict \pm one standard deviation in measurement uncertainty. The fuel/case-specific size distributions are replotted in Figure S2 to S4 to facilitate engine load comparisons.

409 The data also indicate the formation of nucleation mode particles below 20 nm and a
 410 related engine load dependence but are subject to large variability, which makes it dif-
 411 ficult to draw conclusions. Similar size distributions for low FSC fuels from marine test-
 412 bed engines have been reported by Anderson et al. (2015) and Santos et al. (2022).

413 While wet scrubbing maintained the bimodal characteristic of the HiS case, it also
 414 led to a shift in size of the dominant nucleation mode towards larger sizes and a reduc-
 415 tion in the soot mode. A previous study conducted with the same wet scrubber but using
 416 a different engine, showed the formation of a particle mode around 20 nm. There the
 417 authors concluded that this was due to nucleation of sulfur-containing particles (Santos
 418 et al., 2022). However, size distributions for the non-compliant high FSC case, looked
 419 substantially different and lacked the dominant nucleation mode observed in this study.
 420 Similar observations regarding the shift in particle mode between pre- and post-scrubber,
 421 were also made by Jeong et al. (2023), who used a commercially available wet scrubber.
 422 Jeong et al. (2023) came to the conclusion that this shift in the size distribution was due
 423 to coagulation of primary and sulfur-containing particles in the scrubber.

424 Changes in engine load affect the particle size distributions in different ways. Soot
 425 modes are generally reduced in amplitude with increasing engine load as is the count
 426 median diameter of the respective modes with increasing engine load. Although, the lat-
 427 ter observation does not apply to HiS, this deviation may arise from uncertainties in defin-
 428 ing and constraining fitting parameters. While also being largely affected by general vari-
 429 ations in combustion conditions, the amplitudes of nucleation mode particles show a weak
 430 dependence on engine load, where the amplitude slightly increases with increasing load.

431 3.3 Effective Densities

432 In Figure 3 a-c effective densities, ρ_{eff} , obtained from combined AAC and SMPS
 433 measurements, are shown for all cases and identified particle modes. More information
 434 about raw data output and processing, including determination of individual particle modes,
 435 can be found in Figures S8 to S10.

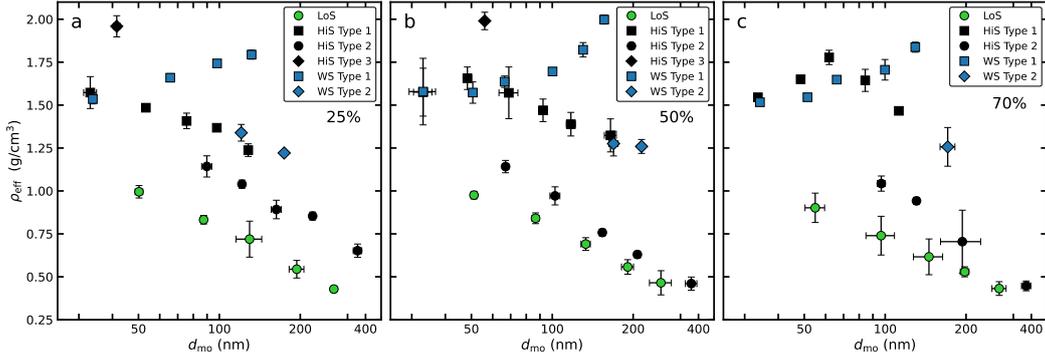


Figure 3. Measured effective densities (ρ_{eff}) for the fuels LoS and HiS and the HiS + wet scrubber case as a function of particle mobility diameter for engine load regimes of (a) 25%, (b) 50% and (c) 70%. Error bars represent \pm two standard deviations. Classification into different particle types was based on observed trends in the raw data output (see Figures S8 to S10). Particle types generally coincide with particle modes in measured size distributions (see Figures 2 and S5 to S7).

436 Effective density values for LoS show a steady decline in ρ_{eff} with increasing mo-
 437 bility diameter (Figure 3). This behavior is typical for soot particles, as the structure
 438 and morphology of exhaust particles become less dense with increasing size, as has been
 439 reported in diesel engine studies (Park et al., 2003; Olfert et al., 2007; Rissler et al., 2013;
 440 Olfert & Rogak, 2019; Trivanovic et al., 2019; Momenimovahed et al., 2021). From the
 441 ρ_{eff} trends, one can derive the mass-mobility relationship according to Park et al. (2003),
 442 where the fractal dimension, D_f , is indicative of the morphology of the exhaust parti-
 443 cles. A homogeneous, spherical particle, for example, has $D_f = 3$, whereas diesel en-
 444 gine exhaust particles typically yield values between 2.2 and 2.8 (Park et al., 2003; Olfert
 445 et al., 2007; Rissler et al., 2013; Trivanovic et al., 2019; Olfert & Rogak, 2019). Anal-
 446 ysis of the mass-mobility relationship for LoS particles (Figure S11) revealed no clear
 447 dependence of D_f on the engine load as the value remains at 2.56.

448 Particles from HiS combustion display different trends in ρ_{eff} compared to LoS. Firstly,
 449 at least three different particle types were classified. The different types remained after
 450 SMPS data were corrected for multiple charging artifacts and also coincide with the dif-
 451 ferent particle modes observed in the measured particle size distributions (HiS; Figure 2
 452 and Figure S6). Effective densities of HiS particles of the first type (up to 165 nm) gen-
 453 erally ranged between 1.24 g cm^{-3} and 1.78 g cm^{-3} between all load points and sizes
 454 and showed no clear trends between 30 nm and 100 nm, making it difficult to assess whether
 455 those are spherical or fractal-like aggregates. Results also indicate a general increase with
 456 engine load. An immediate comparison between LoS and HiS can be drawn when look-
 457 ing at densities values for HiS's second type which shows a significant increase in ρ_{eff}
 458 compared to LoS. Density values of the second type show a clear decreasing trend with
 459 increasing size which indicates a soot mode. Measurements by Olfert et al. (2007) showed
 460 that in the presence of high sulfate concentrations, effective densities could increase dra-
 461 matically due to potential condensation of sulfuric acid which has a material density of
 462 1.84 g cm^{-3} . As for the third observed type, ρ_{eff} varied between $1.96 \pm 0.06 \text{ g cm}^{-3}$ (25%)
 463 and $1.99 \pm 0.05 \text{ g cm}^{-3}$ (50%) which is larger than the density of sulfuric acid but within
 464 the range of the proposed mean value for particles produced from liquid fuels with low
 465 organic content, $1.834 \pm 0.187 \text{ g cm}^{-3}$ (Ouf et al., 2019).

466 Changes in particle number size distributions due to wet scrubbing are also reflected
 467 in ρ_{eff} . Two distinct WS particle behaviors were identified from the analysis and are present
 468 at all three load points. For particles between ≈ 34 and ≈ 130 nm ρ_{eff} increased from 1.56
 469 and 1.82 g cm^{-3} (averaged over all load points). At the low end of this range ≤ 90 nm
 470 the ρ_{eff} WS and HiS values predominantly overlap at the higher load points. At 25%
 471 load HiS and WS results diverge except for the smallest particles (34 nm). Furthermore,
 472 effective density values captured for WS exhaust suggest that the particle types could
 473 potentially be very similar to those emitted from HiS combustion in terms of composi-
 474 tion and morphology. It should be stated, that the type assignment during the analy-
 475 sis steps does not necessarily exclude any misclassification or overlap between types and
 476 size modes, as indicated by the agreement of WS second type particles and the largest
 477 measured effective densities for Type 1 HiS particles.

478 3.4 Chemical Characterization - EDXRF and STXM analysis

Table 2. Summary of particulate matter related emission factors measured for the three dif-
 ferent cases and engine loads normalized by load-dependent fuel consumption. Emission factors
 of S, Cl, K, Ca and Fe were derived from filter-based EDXRF measurements of PM_{2.5} sampled
 using a cyclone impactor. The uncertainties are given as \pm two standard deviations.

Case	Load	S $\mu\text{g kg}^{-1}$	Cl $\mu\text{g kg}^{-1}$	K $\mu\text{g kg}^{-1}$	Ca $\mu\text{g kg}^{-1}$	Fe $\mu\text{g kg}^{-1}$
LoS	25	0.92 ± 0.32	0.10 ± 0.07	0.03 ± 0.02	0.19 ± 0.10	0.33 ± 0.18
	50	0.36 ± 0.13	0.00 ± 0.01	0.00 ± 0.00	0.04 ± 0.02	0.13 ± 0.07
	70	0.18 ± 0.07	0.02 ± 0.01	0.01 ± 0.01	0.02 ± 0.01	0.06 ± 0.04
HiS	25	23.13 ± 5.98	0.03 ± 0.01	0.02 ± 0.01	0.15 ± 0.09	0.33 ± 0.23
	50	20.71 ± 5.89	0.00 ± 0.00	0.05 ± 0.02	0.30 ± 0.10	0.50 ± 0.20
	70	24.91 ± 6.29	0.01 ± 0.01	0.00 ± 0.00	0.09 ± 0.04	0.40 ± 0.14
WS	25	38.63 ± 9.45	1.25 ± 0.32	0.14 ± 0.09	0.51 ± 0.17	0.51 ± 0.25
	50	38.23 ± 9.70	0.95 ± 0.28	0.32 ± 0.10	0.66 ± 0.19	0.62 ± 0.18
	70	31.14 ± 8.39	0.60 ± 0.16	0.07 ± 0.04	0.31 ± 0.09	0.93 ± 0.29

479 Table 2 summarizes emission factors normalized by fuel consumption for selected
 480 elements derived from EDXRF analysis of PM_{2.5} filters. Emissions of sulfur are signifi-
 481 cantly reduced at lower FSCs. Since the fuel compositions of HiS and LoS mainly vary
 482 in terms of sulfur content and engine parameters for various engine load points were repli-
 483 cated for all cases, we can conclude that the difference in sulfur emissions is mainly driven
 484 by enhanced emissions of sulfur containing particles when using HiS fuel, either due to
 485 nucleation of new particles containing sulfur species or due to coating of soot particles.
 486 The sulfur in the LoS case may originate from the relatively small amount of FSC or a
 487 potential non-negligible sulfur content in the lubrication oil. Sulfur emission factors in
 488 the particulate phase are increased when HiS exhaust is passed through the wet scrub-
 489 ber. While no load dependence is apparent, particle sulfur emissions are increased on
 490 average by 59% when the scrubber is used. This result supports the hypothesis, that the
 491 scrubbing can lead to coagulation of nucleated sulfur-containing particles or lead to en-
 492 hanced surface uptake of sulfur species by primary exhaust particles. These results agree
 493 with observations made by Yang et al. (2021), who found wet scrubbing to be inefficient
 494 in removing sulfate particles, and Jeong et al. (2023), who observed coagulation of sul-
 495 fate particles downstream of a wet scrubber. We cannot exclude the presence of other
 496 sulfur-containing particles not captured by the SMPS measurements.

497 Wet scrubbing was also found to enhance emissions of chlorine, potassium, calcium
 498 and iron. While the chlorine, potassium and calcium are linked to the composition of
 499 the seawater used for the scrubbing process, enhanced iron concentrations may have orig-
 500 inated from corrosion of scrubber and or exhaust-pipe components. We cannot exclude
 501 the potential for scrubbing processes to lead to enhanced external mixing of particulate
 502 or to influence microphysical processes affecting chemical compositions.

503 Other elements that are often used as tracers for different fuel types, such as vana-
 504 dium for high FSC residual fuel oils (Popovicheva et al., 2009; Moldanová et al., 2009;
 505 Moldanová et al., 2013), were either found to be around background levels or below de-
 506 tection limits in all cases.

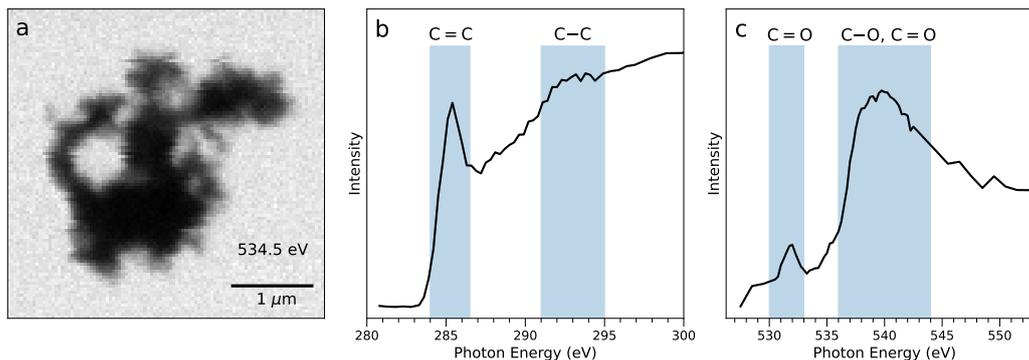


Figure 4. A scanning transmission X-ray microscopy (STXM) image and corresponding near-edge absorption fine structure (NEXAFS) spectra of a typical LoS exhaust particle. (a) A X-ray microscopy image taken of the respective particle at the oxygen K-Edge at 534.5 eV. NEXAFS spectra acquired for the particle at (b) the carbon K-edge and (c) the oxygen K-edge. The blue shaded areas in panel (b) and (c) mark absorption features related to the different functional groups displayed over the corresponding areas. The ranges for the shaded areas were visually estimated from Moffet et al. (2010).

507 Complimentary STXM and NEXAFS analyses show that different cases resulted
 508 in different mixing states characterized by a few distinct particle types. For LoS sam-
 509 ple grids mainly carbonaceous, soot like particles were observed, although we cannot fully
 510 exclude that other combustion-related particles are present. Figure 4 shows (a) a typ-
 511 ical soot particle and corresponding NEXAFS spectra at (b) the carbon K-edge and (c)
 512 the oxygen K-edge. The peak observed at ≈ 285.4 eV is characteristic for the sp² hybridized
 513 carbon transition (doubly bonded carbon) which is also referred to as a “graphitic peak”
 514 and has been documented for soot particles from different combustion sources (Braun,
 515 2005; di Stasio & Braun, 2006; Moffet et al., 2010; Alpert et al., 2017; Mahrt, Alpert,
 516 et al., 2020). A broad absorption feature starting at around 291 eV is characteristic of
 517 the C–C single bond. The oxygen K-edge shown in panel c indicates the presence of the
 518 carbonyl group in the particle as indicated by the sharp and broad peaks at ≈ 531 eV
 519 and ≈ 538 eV respectively (Tivanski et al., 2007; Moffet et al., 2010).

520 For HiS exhaust, two distinct particle compositions were observed which were iden-
 521 tified as soot and sulfate (Figure 5 a). In the Figure 5 b the soot NEXAFS spectrum has
 522 a peak at around 532 eV corresponding to the carbonyl group, which is missing for the
 523 sulfate. Both spectra show a distinct σ^* resonance peak above 537 eV, which signals the
 524 presence of sulfate (Zelenay et al., 2011; Fauré et al., 2023; Kong, Gladich, et al., 2023).
 525 This peak is broader for the soot particle, which indicates the presence of oxygen atoms

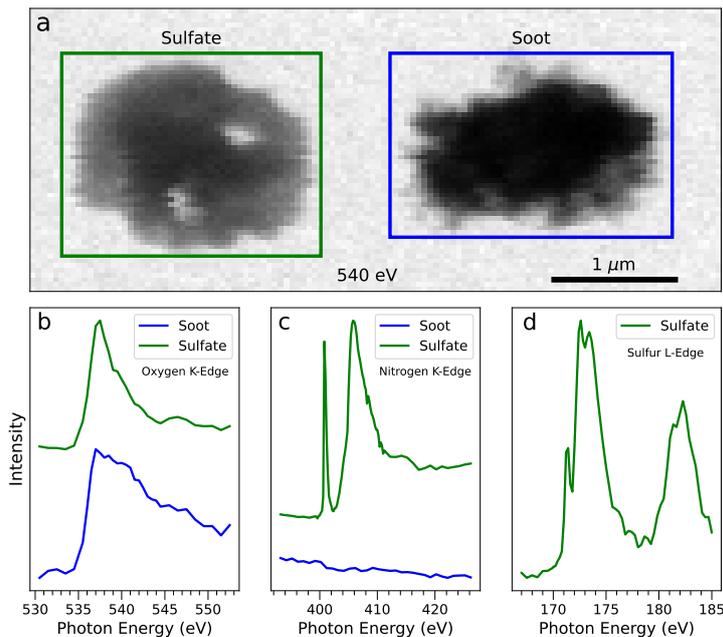


Figure 5. STXM image and NEXAFS spectra from HiS exhaust particles. (a) STXM images taken at 540 eV showing sulfate-type and soot particles. NEXAFS spectra at (b) the oxygen K-edge, (c) the nitrogen K-edge and (d) the Sulfur L-edge. Spectra shown in panels (b) to (d) represent the average of whole particles, although during the analysis process all particles were inspected for spectral heterogeneity.

526 bonded to carbon atoms but other compounds cannot be excluded due to the complex-
 527 ity of this absorption region. The nitrogen K-edge spectrum for the sulfate particle shows
 528 two distinct absorption features which have been previously observed for ammonium sul-
 529 fate particles by Leinweber et al. (2007), although presence of nitrate in the nitrogen K-
 530 edge spectrum of the sulfate particle cannot be excluded (Weeraratna et al., 2022; Kong,
 531 Priestley, et al., 2023). No nitrogen was associated with the soot particle. The sulfur L-
 532 edge spectrum of the sulfate particle (Figure 5 c) shows characteristic peaks between 170
 533 eV and 185 eV which align with those measured for sodium sulfate particles by Sarret
 534 et al. (1999). Experimental constraints did not allow for a sulfur spectrum to be acquired
 535 for HiS soot particles but a direct comparison of oxygen K-Edge spectra between the LoS
 536 and HiS soot particles (Figures S13) shows distinct spectral differences between 536 eV
 537 and 539 eV. The oxygen spectrum of the HiS soot particle shows a sharp increase in absorp-
 538 tion at ≈ 536 eV which coincides with the spectrum of the HiS sulfate particle. For
 539 the LoS soot particle, a similar absorption feature is shifted towards higher energies of
 540 ≈ 538 eV. Similar variations in oxygen NEXAFS spectra for fresh soot and sulfuric acid
 541 aged soot have been observed. There, the authors conclude that the shift in signal to-
 542 wards lower energies for the aged soot originates from sulfate on the soot particle (Priestley
 543 et al., 2023).

544 In Figure 6 a an overview snapshot of WS particles at a single energy of 285.8 eV
 545 (carbon absorption edge), displays different particle types, which were consistent for all
 546 WS samples. A differential image, which was produced by aligning two images of dif-
 547 ferent energies (pre- and post- sodium K-edge) and subtracting the signal of the pre-edge
 548 image from the post-edge signal (Figure 6 b; 1071 - 1065 eV) highlights the presence of
 549 cubic-shaped sodium chloride particles. A similar image at the oxygen K-edge (537.5 -

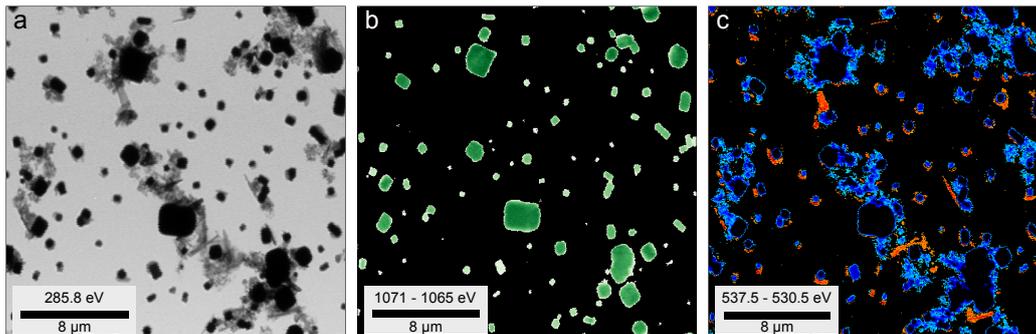


Figure 6. STXM images of particles from wet scrubber exhaust taken at different energies. (a) Single energy image around the carbon K-Edge (285.8 eV) showing different particle morphologies present on the grid. (b) Differential energy image at the sodium K-Edge (1071 eV - 1065 eV), where different shades of green indicate the intensity of the measured Na signal. (c) Differential energy image at the oxygen K-Edge (537.5 eV - 530.5 eV), where hues of red indicate the presence of oxygen-rich sulfates and mineral particles and bluish hues highlight oxygen-containing soot particles. In (b) and (c) images taken within the same absorption edge were pixel-aligned and background corrected. Signals of the lower (pre-edge) energies were subtracted from signals obtained at absorption peaks (higher energy values). The choice of the two respective energy values were based on carbon and sodium NEXAFS spectra typical for the respective particle types.

530.5 eV; Figure 6 c) shows fractal-like, oxygen containing particles highlighted in blue and column-shaped mineral particles (calcium sulfate, CaSO_4), as well as other oxygen-containing particles in orange. In the WS samples, isolated soot or mineral particles were rarely observed and often surround salt particles. One explanation for this is that the aforementioned particles were immersed in saline solution droplets during the sampling process. The water subsequently evaporated during storage or STXM analysis, leaving behind crystallized salt particles with attached soot and mineral particles. Similar heterogeneous particle mixtures have been observed in exhaust utilizing the same scrubber but with a different engine (Santos et al., 2023). Similar to HiS emissions, sulfate particles were also encountered for the WS case (see Figure S14).

3.5 CCN Activity

The calculated hygroscopicity parameter, κ , for all cases, engine loads and particle sizes between 50 nm and 250 nm is displayed in Figure 7. Combustion of HiS fuel resulted in emissions of particles with relatively high hygroscopicities. The κ value of 50 nm particles varied between 0.661 and 0.649 with no apparent engine load trend. These values are comparable to those of sulfur-containing, inorganic species, such as ammonium sulfate, which has a κ -value of 0.61 (Petters & Kreidenweis, 2007) and to those of exhaust particles from ships utilizing fuels with a FSC > 0.5%, which has been estimated to be around 0.63 (Yu et al., 2020, 2023). In general, the hygroscopicity of HiS exhaust particles decreases with increasing particle size. However, at 75 nm, κ values are substantially smaller than for 50 nm or 100 nm particles. This may be due to an overlap of different particle types of varying hygroscopicity, which could not be clearly resolved in the activation spectra. Beyond 100 nm a steady decrease in κ is observed with increasing particle size, which supports the hypothesis that particle emissions around 50 nm and larger than 100 nm are dominated by emissions of sulfate and soot respectively.

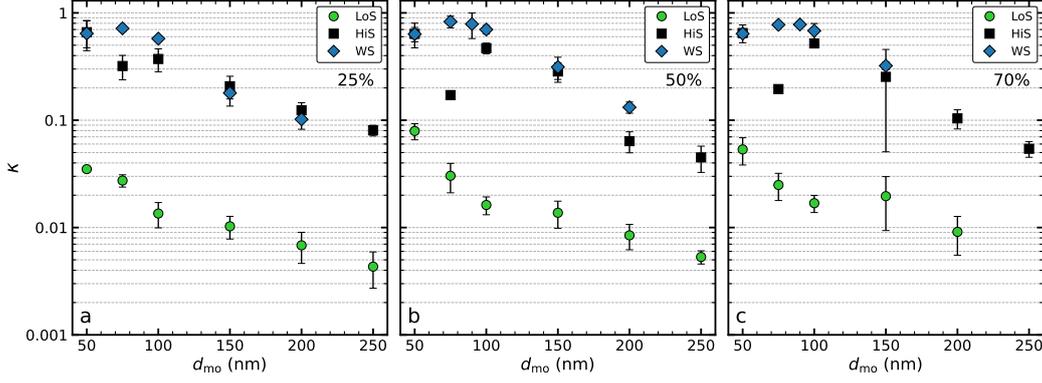


Figure 7. CCN activity expressed as the mean hygroscopicity parameter (κ) value for particle mobility diameters between 50 and 250 nm. LoS represents combustion of low FSC fuel, HiS of non-compliant high FSC fuel and in WS, HiS exhaust was processed by the wet scrubber. Panels (a) to (c) show results for engine loads ranging from 25% to 70% (as indicated). The error bars represent \pm two standard deviations of measurement uncertainty. All κ values were calculated from measured critical supersaturations (see Figure S15).

575 The hygroscopicity of exhaust particles is strongly affected by FSC reduction as
 576 can be seen from the significantly reduced κ values of LoS particles. At 50 nm, κ is re-
 577 duced to 0.035 - 0.079. These hygroscopicities agree with measurements from other diesel
 578 engine studies of unaged soot particles (Henning et al., 2012; Wittbom et al., 2014; Ko-
 579 ronen et al., 2022). The strong reduction in hygroscopicity compared to HiS was ob-
 580 served for all measured particle sizes as κ continues to decrease monotonically with in-
 581 creasing particle size. The large difference in κ between HiS and LoS can be explained
 582 by the absence of sulfate particles and sulfate on soot particles, which can increase hy-
 583 groscopicity of generally hydrophobic soot particles. No clear correlation between hy-
 584 groscopicity and engine load was found.

585 The effect of wet scrubbing on κ values is mostly seen in the size range 50 nm to
 586 100 nm. These changes also coincide with the shifts in the dominant particle modes to-
 587 wards larger sizes which is shown in Figure 2 and the changes in ρ_{eff} for WS particles
 588 (Figure 3). For all three engine loads, the hygroscopicities of WS particles between 50
 589 nm and 100 nm did not display any clear size-dependence. The average values for this
 590 size range vary between 0.65 and 0.74 with no clear engine load dependence. It was found
 591 that the κ values of 50 nm WS particles were very similar to those of 50 nm particles
 592 originating from HiS combustion. Taking into account the similarities in ρ_{eff} for the same
 593 size range and the results obtained from the chemical characterization, we can hypoth-
 594 esize that 50 nm particles in both cases are similar. Above 100 nm, κ values of WS par-
 595 ticles decrease steadily to values of 0.102 (25%) and 0.132 (50%) at 200 nm. These re-
 596 sults suggest, wet scrubber particle emissions on the submicron scale are dominated by
 597 at least two distinct particle types, that is, hygroscopic sulfate particles and chemically
 598 altered soot particles.

599 3.6 IN Activity

600 Onset conditions for ice nucleation at a given temperature and relative humidity
 601 with respect to ice, RH_i , for 50% engine load experiments are presented in Figure 8. The
 602 onset conditions were determined when activated fractions exceeded 1%, determined by
 603 calculating the ratio between the sum of all OPC channels $\geq 3 \mu\text{m}$ and the total par-

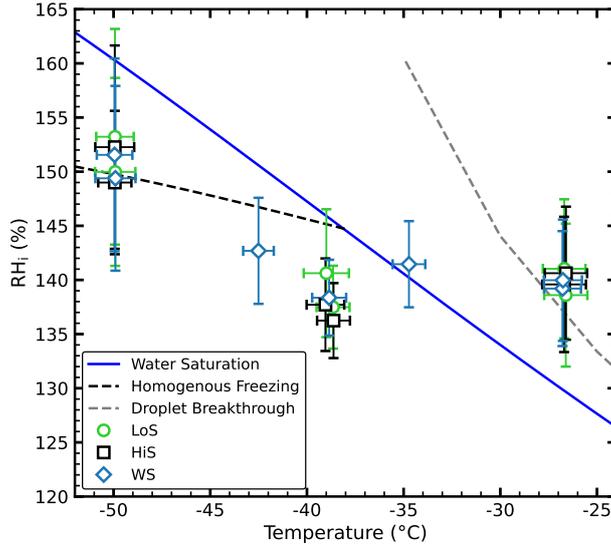


Figure 8. Summary of 200 nm particle freezing experiments over a range of -50°C to -26°C . Freezing onsets were determined where the frozen fraction between ice crystals ($> 3 \mu\text{m}$) and the total particle number concentrations exceeded 1%. The solid blue line indicates water saturation, the dashed blue line represents the homogeneous freezing threshold for 200 nm particles according to Koop et al. (2000) (calculated with a water activity (Δa_w) of 0.2946) and the grey dashed line represents the experimentally determined droplet breakthrough conditions of PINCii (Castarède et al., 2023).

604 ticle numbers detected by the CPC measuring in parallel with PINCii. In contrast to
 605 the results obtained from CCN activity measurements, ice nucleation onsets do not vary
 606 with fuel type or exhaust wet scrubbing. At temperatures warmer than required for ho-
 607 mogeneous freezing, ice nucleation was not observed below water saturation. Data col-
 608 lected at around -26°C show that all onsets are around droplet breakthrough conditions
 609 (grey dashed line), which was experimentally determined for various PINCii operating
 610 conditions by Castarède et al. (2023). This line indicates a threshold in T - RH_i param-
 611 eter space wherein unfrozen droplets continue to grow to detectable sizes for the OPC,
 612 thus inhibiting phase discrimination. At temperatures between $\approx -34^{\circ}\text{C}$ and -43°C , freez-
 613 ing onset occurs below homogeneous freezing conditions, which has previously been re-
 614 ported for soot particles coated with different acids (Friedman et al., 2011) and agrees
 615 with measurements by (Möhler et al., 2005). In Santos et al. (2023), the authors found
 616 that the fuel aromatic content had a major influence on the exhaust particles' ability to
 617 form liquid droplets. It is therefore possible that aromatics may also facilitate freezing
 618 of fresh soot particles. Organics and sulfuric acid in the particle phase can have a large
 619 influence on the IN ability of soot particles, for example, by filling pores and thus, in-
 620 hibiting pore condensation freezing, or by increasing particles' hygroscopicities due to
 621 sulfuric acid coatings (Gao & Kanji, 2022).

622 If wet scrubbing of exhaust particles is seen as a type of cloud conditioning, then
 623 it might enable heterogeneous freezing at warmer temperatures and/or lower supersat-
 624 urations as has been demonstrated by Mahrt, Kilchhofer, et al. (2020). Nevertheless, un-
 625 certainties in RH_i are pronounced, making it difficult to determine precisely the RH of
 626 the freezing onsets. It is also worth noting that at $T = -50^{\circ}\text{C}$ ice crystal growth of 200
 627 nm sample particles to sizes above $3 \mu\text{m}$ is significantly limited by the residence time in-
 628 side PINCii's growth chamber and requires RH_i above 150% (Figure S16). This can in-

Table 3. Summary of particulate matter related emission factors measured for the three fuel cases and engine loads normalized by load-dependent fuel consumption. Particle number (EF_{PN}) and particle mass emission factors (EF_{PM}) are derived from integration of measured particle size distributions between 11 and 470 nm. Moreover, EF_{PM} are calculated (1) assuming unit density for all particles (EF_{PM,ρ_0}) and (2) using the average ρ_{eff} for individual particle modes ($EF_{PM,\rho_{\text{eff}}}$). The uncertainties are given as \pm two standard deviations.

Case	Load	EF_{PN} $10^{14} \# \text{ kg}^{-1}$	EF_{PM,ρ_0} (1) mg kg^{-1}	$EF_{PM,\rho_{\text{eff}}}$ (2) mg kg^{-1}	$EF_{CCN,0.3\%}$ $10^{13} \# \text{ kg}^{-1}$	$EF_{CCN,0.7\%}$ $10^{13} \# \text{ kg}^{-1}$
LoS	25	1.18 ± 0.04	84.70 ± 3.20	62.49 ± 2.36	0.20	1.13
	50	0.73 ± 0.23	48.76 ± 14.75	34.70 ± 10.50	0.18	0.75
	70	0.33 ± 0.33	16.88 ± 3.29	11.08 ± 2.16	0.08	0.29
HiS	25	69.90 ± 8.90	181.92 ± 28.94	198.23 ± 32.08	7.19	51.76
	50	80.68 ± 14.55	111.23 ± 21.91	126.01 ± 28.73	3.22	33.27
	70	77.52 ± 30.11	116.35 ± 30.50	164.58 ± 44.30	1.76	77.32
WS	25	26.93 ± 5.11	238.48 ± 63.26	388.36 ± 105.96	43.22	146.75
	50	23.44 ± 2.73	201.14 ± 18.62	333.14 ± 31.17	38.77	136.26
	70	28.19 ± 4.83	218.20 ± 18.25	358.92 ± 30.05	45.41	166.25

629 introduce an additional uncertainty when performing measurements at low temperatures.
630 In Castarède et al. (2023), the authors show an alternative way to visualize freezing on-
631 sets of aerosol particles using PINcii. This approach takes into account the fact that ho-
632 mogeneous freezing is an irreversible process. Once ice formation is triggered, ice crys-
633 tals continue to grow even if their remaining trajectory inside the growth chamber has
634 less favorable freezing conditions. Here, we employ this alternative method to determine
635 freezing onsets based on maximum RH_i values in the flow lamina. Results utilizing this
636 alternative approach are presented in Figure S17 and suggest that most data reflect ho-
637 mogeneous or even more extreme freezing conditions.

638 3.7 Emission Factors - PN, PM and CCN

639 Emission factors normalized by fuel consumption for particles derived from SMPS
640 measurements (11 nm to 470 nm) are shown in Table 3. In general, particle number emis-
641 sion factors (EF_{PN}) varied between $0.33 \times 10^{14} \text{ kg}^{-1}$ and $80.68 \times 10^{14} \text{ kg}^{-1}$. A strong
642 reduction in EF_{PN} was observed when switching from non-compliant HiS to SECA-compliant
643 LoS, which agrees with other studies that have shown large reductions in particle num-
644 ber emissions due to FSC reductions (Seppälä et al., 2021; Yu et al., 2020, 2023; Wu et
645 al., 2020). On average EF_{PN} were reduced by 99%, which can be largely attributed to
646 the absence of sulfate aerosol smaller than 50 nm. Nevertheless, soot mode particles were
647 also reduced when using LoS fuel (see Figure 2). During WS experiments emissions were
648 on average reduced by 65% compared to HiS which is within the range of other stud-
649 ies investigating the effects of wet scrubbers on PN emissions from marine engines (Fridell
650 & Salo, 2016; Winnes et al., 2020; Lehtoranta et al., 2019; Yang et al., 2021). Contrast-
651 ingly in a previous study, that utilized the same scrubber but a different engine, wet scrub-
652 bing led to an increase in EF_{PN} (Santos et al., 2022). The change in emission behavior
653 compared to Santos et al. (2022) may have different sources, including general differences
654 in the emission profiles between engines or the addition of packing material between scrub-
655 ber demister plates that was not utilized in the earlier study. A clear load dependence
656 was only observed for LoS where EF_{PN} are steadily reduced with increasing engine load.

657 Particle mass emission factors show diverging trends for the alternative compliance
658 measures. For LoS fuel, EF_{PM} are reduced on average by 65% and 75% when either as-

659 suming unit density for all particles (EF_{PM,ρ_0}) or when using average ρ_{eff} values for in-
 660 dividual particle modes ($EF_{PM,\rho_{\text{eff}}}$). Wet scrubbing led to a reduction in particle num-
 661 bers but EF_{PM,ρ_0} and $EF_{PM,\rho_{\text{eff}}}$ increased by 67% and 126% compared to the respec-
 662 tive HiS cases. As can be seen in Figure 2, scrubbing led to a decrease in the soot mode
 663 but this removal of large particles is compensated by the shift in the ultrafine, sulfate
 664 mode. Similar to EF_{PN} results, a clear engine load dependence was only observed for
 665 LoS where emissions decrease with increasing engine load.

666 The importance of including particle type differences and morphologies when es-
 667 timating EF_{PM} from SMPS measurements is highlighted when the differences for indi-
 668 vidual cases are compared. For the soot particles that are emitted from LoS combustion,
 669 decreasing trends in ρ_{eff} are reflected in reduced EF_{PM,ρ_0} . On the other hand, sulfates,
 670 salts and generally more dense particles, have material densities larger than 1 g cm^{-3}
 671 and often do not possess fractal structures like soot particles, thus leading to relative in-
 672 creases in EF_{PM} for HiS and WS.

673 Estimated CCN emission factors (EF_{CCN}) for atmospherically relevant supersat-
 674 urations of 0.3% and 0.7% are shown in Table 3. The full spectrum of EF_{CCN} for a su-
 675 persaturation range of 0% - 1% is shown in Figure S18. During the interpolation pro-
 676 cess to derive size-dependent critical supersaturation values of HiS particles, κ values at
 677 75 nm were excluded due to the previously discussed uncertainties.

678 Estimates show different EF_{CCN} trends for the competing compliance pathways when
 679 compared to HiS. At both $SS = 0.3\%$ and 0.7% CCN emissions are substantially reduced
 680 for LoS across all load points. On average CCN emissions are reduced by 97% due to
 681 the switch to the low FSC fuel for both SS values with little variation across engine loads.
 682 Similar CCN reductions from ships operating on low FSC fuels were observed by Yu et
 683 al. (2020, 2023). Wet scrubbing, on the other hand, was found to lead to a substantial
 684 increases in EF_{CCN} when compared to HiS. Compared to a previous study conducted
 685 with the same scrubber where no clear increase in CCN emissions was found (Santos et
 686 al., 2023), here, scrubbing induced shifts in the particle size distributions towards larger
 687 sizes, strongly impact EF_{CCN} . While κ values for HiS and WS are similar and and par-
 688 ticles larger than ≈ 200 nm are reduced from scrubbing, the increase in CCN emissions
 689 for the WS case is dominated by substantially increased particle concentrations in the
 690 range of 50 nm to 100 nm.

691 4 Summary and Implications

692 In this study, a diesel engine was used to investigate how present international ma-
 693 rine fuel regulations impact physicochemical properties and the cloud activity of exhaust
 694 particles. We investigated two regulatory compliance measures aimed at sulfur emission
 695 reductions. Those are, direct fuel sulfur content reduction and exhaust wet scrubbing.
 696 Aerosol instrumentation was used to measure size distributions and effective densities
 697 of emitted exhaust particles as well as their liquid droplet and ice crystal forming abil-
 698 ities. Energy dispersive X-ray fluorescence and scanning transmission X-ray microscopy
 699 were used to characterize chemical compositions and exhaust particle mixing states. This
 700 study found that compliance measures have significant impacts on particulate emission
 701 profiles with relevant implications for atmospheric processes and human health. Our key
 702 findings are:

- 703 • Combustion of low sulfur content fuel resulted in significant reductions of ultra-
 704 fine particulate emissions, most likely due to the absence of sulfate particles in the
 705 range of 20 nm to 30 nm. In this case, particulate emissions are dominated by soot
 706 particles.

- 707 • While soot mode particles were reduced, wet scrubbing was found to shift sulfate
708 mode particles towards larger sizes, possibly due to coagulation. This shift in the
709 sulfate mode is supported by results from EDXRF measurements, where we see
710 significant increases in particulate sulfur emissions from wet scrubbing compared
711 to the non-compliant fuel.

- 712 • Changes in the mixing state of the particles are also reflected in their hygroscop-
713 icities. Low sulfur fuel combustion primarily led to particle emissions of low hy-
714 groscopicity, resulting in strong CCN emission reductions compared to non-compliant
715 high sulfur content fuel. Wet scrubbing, on the other hand, increased CCN emis-
716 sions substantially, most likely caused by changes in the particle size distributions
717 and/or due to possible transfer and condensation of water-soluble compounds onto
718 exhaust soot particles.

- 719 • While we found compliance measures affect exhaust particles hygroscopicities', no
720 significant impact on ice nucleation was observed. Potential changes in the mix-
721 ing state of 200 nm wet scrubber exhaust particles, did not improve ice nucleation
722 abilities of particles. Fresh soot-type particles remain inefficient ice nucleating par-
723 ticles.

- 724 • With the exception of particle size distributions and consequently, particle num-
725 ber and mass emission factors, no obvious engine load dependencies were found
726 for other parameters, such as the effective densities and the CCN activity of ex-
727 haust particles. We observed that soot mode particles are clearly reduced with in-
728 creasing engine load. This was not the case for sulfates within the ultrafine mode.

729 Despite efforts to reduce particulate emissions to the atmosphere, maritime trans-
730 port remains a significant source. A variety of fuel types and exhaust aftertreatment sys-
731 tems are emerging, as marine regulations evolve. Studying these emissions remains an
732 important research question. This study shows that two alternative solutions to com-
733 ply with emission control regulations have significant impacts on properties of exhaust
734 particles. These types of results have implications for human health, for example, by re-
735 ducing or increasing the burden of submicron particle emissions close to populated ar-
736 eas, affected by ship traffic, but can also have climate related consequences. While we
737 only studied those effects on fresh exhaust particles, once emitted to the atmosphere, par-
738 ticles undergo chemical and physical processing that can influence their interaction po-
739 tential within the atmosphere (Khalizov et al., 2009; Wittbom et al., 2014; Mahrt, Alpert,
740 et al., 2020). The Arctic is an interesting study area, where unprecedented feedback mech-
741 anisms lead to amplified warming rates and to steadily decreasing sea ice extent. Increas-
742 ing shipping activity is a projected future result (Peters et al., 2011). In such pristine
743 environments, where background aerosol concentrations are generally low, aerosol intro-
744 duced by ships may cause strong local responses in the Earth-atmosphere system. An-
745 ticipating potential risks posed by growing shipping activity, ongoing initiatives are fo-
746 cused on reducing its environmental footprint. For example, from 2024 and onwards ships
747 in the Arctic will no longer be allowed to use heavy fuel oils or, in general, fuels with den-
748 sities and kinematic viscosities exceeding 900 kg m^{-3} and $150 \text{ mm}^2 \text{ s}^{-1}$ respectively (IMO,
749 2021a). Regulations like these will most likely reduce wet scrubber usage in the Arctic
750 and also alter exhaust emissions of particulate matter from ships in Arctic waters. To
751 this day, large uncertainties in quantifying aerosol-cloud interactions and especially, the
752 effect of maritime shipping on radiative forcing, still prevail (IPCC, 2021). The results
753 presented in this study, including information on exhaust particle size distributions, as-
754 sociated hygroscopicity values and emission factors, can be useful input parameters for
755 cloud-resolving boundary layer models to investigate the potential impact of ship emis-
756 sions on cloud properties and their effects on the climate system. This may not only im-
757 prove our general understanding of ship aerosol cloud interactions but also help in as-
758 sessing the impact of Arctic based shipping activity.

Open Research Section

The data has been submitted to the Swedish National Data Service, an open access database. This section will be updated with a DOI once the data submission has been approved.

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