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(Citation)
Chemosphere,223:399-405

(Issue Date)
2019-05

(Resource Type)
journal article

(Version)
Accepted Manuscript

(URL)
https://hdl.handle.net/20.500.14094/90005679

Identifying sulfur species adsorbed on particulate matters in exhaust gas emitted from various vessels

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Highlights

- Sulfur species adsorbed on PM in ship exhaust gas were identified.
- The sulfur species of PM did not change between high and middle loads.
- Sulfate, sulfite, sulfonate, and thiophen were identified in PM and soot.
- Sulfonate was derived from fuel or oxidation of sulfide in fuel.
- Sulfate in soot increased with increasing sulfur content in fuels.

Abstract

Ship fuels are highly associated with the emission of particulate matter and sulfur. Sulfur adsorbed on particulate matter in exhaust gases from fuels is generally considered to be sulfate. However, other chemical species of sulfur adsorbed on particulate matter in ship exhaust gases are not well known. The purpose of this study is to identify sulfur species adsorbed on particulate matter in ship exhaust gases using X-ray absorption fine structure. Particulate matter and soot samples were collected from a container carrier, a tugboat, an electric propulsion vessel, training vessels, and a marine engine, and sulfur species of particulate matter and soot were identified by X-ray absorption fine structure analysis. Sulfur emission adsorbed on particulate matter and sulfur species did not change between high and middle loads. In this study, sulfonate derived from fuel or oxidation of sulfide in fuel was identified in addition to sulfate. Total sulfur and sulfate concentrations in soot increased with increasing fuel sulfur content. The concentration of organosulfurs in soot such as thiophen and sulfonate, which originated mainly from fuel and engine oil, tended to increase with increasing fuel sulfur content.

Key Words

distillate marine fuel, gas oil, ship diesel engine, sulfonate, sulfate, thiophen

1. Introduction

Particulate matter (PM) from seagoing ships affect the ocean environment on various scales. Increasing arctic shipping activities coupled with the decline of the arctic sea ice have intensified this effect, resulting in increased environmental impact on the arctic (Schröder et al., 2017). Emission of nitrogen oxides (NO_x) and sulfur oxide (SO_X) adsorbed on PM in exhaust gases is responsible for acid rain. Additionally, PM and sulfur can have an indirect effect on climate through changes in global radiative forcing (Capaldo et al., 1999). Approximately 80% of the fuel used in commercial shipping in 2007–2011 was low-grade, high-sulfur content fuel (Smith et al., 2015). Therefore, it is assumed that combustion of ship fuel emits sulfur as SO_x (SO_2 and SO_3) with other exhaust gases. Because the lifetime of sulfur species in the atmosphere is short (days to about a week), the acid deposition occurs on land and in the ocean (Doney et al., 2007). The SO_x is also partially adsorbed as sulfate onto PM through hydration processes, due to the decrease in temperature of exhaust gas.

The estimated annual PM emission from ships is 0.9-1.7 million tons (Moldanová et al., 2009). Sulfate and PM emissions increased with increasing fuel sulfur content (Agrawal et al, 2008a). Moreover, the particle emission factor and particle number were correlated with SO_2 emission factor (Alföldy et al., 2013; Mousavi et al., 2018). Given

91 that PM and sulfur emission is closely linked to the sulfur content of ship fuels, in 2015
92 the International Maritime Organization (IMO) introduced regulations that the sulfur
93 content in ship fuel be less than 3.5% and 0.1% for general and designated sea areas,
94 respectively. In 2020, the regulation will be further strengthened to reduce sulfur content
95 in ship fuel to 0.5% for general sea areas (Endres et al., 2018). The amount of SOx emitted
96 from seagoing ships has conventionally been estimated by emission factors based on
97 sulfur content in fuels (Tzannatos 2010; Berechman, and Tseng, 2012; Endresen et al,
98 2005). However, the chemical species of sulfur adsorbed on PM in exhaust gases are not
99 well known, which is an impediment to establishing appropriate regulations for sulfur
100 emission control from ships. Sulfur adsorbed on PM in exhaust gases from fuels is
101 considered to be sulfate (Moldanová, et al. 2009). Unlike automobiles, however,
102 oxidation catalysts are not used for ship exhaust gas treatment processes.
103 Conventionally, sulfur adsorbed on PM is extracted and sulfate concentrations
104 analyzed (Agrawal et al, 2008b; Querol et al., 2001; Mueller et al., 2015; Ostro et al,
105 2011). Despite the widespread use of this method, such extractions bear a risk of
106 misinterpretation due to oxidation of the sulfur species during the extraction procedures.
107 However, it is necessary to understand the concentration of each sulfur species of PM
108 emitted from ships to grasp the chemical transformation and equilibrium processes of

109 sulfur adsorbed on PM, and to evaluate the environmental impact based on solubility.

110 In this study, we used X-ray absorption fine structure (XAFS) spectroscopy to identify
111 sulfur species adsorbed on PM and soot. XAFS has been used to identify chemical species
112 with minor or no pretreatments, and thus it offers a great advantage in terms of keeping
113 the sulfur species adsorbed on the PM. XAFS has been applied to the analysis of the
114 chemical form and oxidation state of sulfur in PM from fossil fuels (Huggins and Huffman,
115 2002), diesel PM (Huggins et al., 2000), engine motor oils (Lützenkirchen-Hecht et al.,
116 2014), and exhaust particles emitted from auto engines (Mölders et al., 2001). However,
117 chemical species of sulfur adsorbed on PM in ship exhaust gases are not well known. In
118 this study, PM or soot samples were collected from a container carrier, a tugboat, a
119 research and training electric propulsion vessel, and training vessels. The purpose of this
120 study is to identify sulfur species adsorbed on PM or soot emitted from various vessels.

121

122 **2. Experimental**

123 **2.1 Effect of fuel sulfur content on sulfur species adsorbed on PM**

124 Distillate marine fuel (DMX; sulfur content 0.08%) and sulfur-added fuel prepared
125 from mixing di-t-butyl disulfide with the DMX at 3.5 or 5% by sulfur weight were directly
126 injected into a four-stroke diesel engine (Yanmar NFD13-ME; single cylinder; cylinder

127 volume: 638 cm^3; compression ratio: 17.7; rated output: 6.2 kW at 2000 rpm). The engine
128 was operated under 75% load, with an injection valve pressure of 19.6 MPa. A sampling
129 nozzle for collecting PM from the engine exhaust gas was connected directly to an
130 exhaust gas pipeline from the engine. PM in the exhaust gas was collected with a glass
131 fiber filter (PG-60; Advantec) as 10 L of the gas was introduced into a filter manifold
132 attached with a Liebig condenser by an air pump at flow rate of 12 L min^{-1}. The exhaust
133 gas temperature was controlled to approximately 50 ^oC by the Liebig condenser at the
134 filter manifold. After the PM was collected, the filter samples were dried at 100 ^oC for 6
135 h. The PM mass collected on the filter was calculated by weight difference before and
136 after the exhaust gas was introduced. In the case of filter samples for XAFS analyses,
137 samples were stored immediately in a vacuum packing bag and stored in a freezer to
138 maintain chemical species of sulfur until XAFS analyses.
139 The SO_2 concentration in the exhaust gas was measured with an exhaust gas analyzer
140 (testto 350; Nippon Sokki). Multiple-comparison analyses were carried out to detect
141 significant differences in the obtained data by Fisher's least significant difference method
142 using the statistical software Excel-Toukei (BellCurve).
143

144 **2.2 Collecting PM and soot from the exhaust gas of various ships**

PM samples were collected from the container carrier EMERALD I (Aoki Marine Co., Ltd.), the tugboat KASUGA-MARU II (Maruei Co., Ltd.), the research and training electric-propulsion vessel TOYOSHIO-MARU (Hiroshima University), the training vessel HIROSHIMA-MARU (National Institute of Technology, Hiroshima College), and the training vessel FUKAE-MARU (Kobe University). The specifications and a photo of each vessel are presented in **Table 1 and Fig. S1**, respectively. The sampling nozzles used to collect PM in the engine exhaust gas from the EMERALD I or FUKAE-MARU were connected directly to an exhaust funnel. PM in the exhaust gas was collected with a glass fiber filter (PG-60; Advantec) by letting 10–60 L of exhaust gas pass through the filter by an air pump at a flow rate of 12 L min^{-1} and into the filter manifold chamber attached with a Liebig condenser. The exhaust gas temperature was controlled at approximately 50 ^{o}C by the Liebig condenser at the filter manifold.

Soot samples were also collected by scraping the ship funnels. The measurement of PM mass and preservation of the filter samples for XAFS analyses were conducted as described in section 2.3.

2.3 Analyses of sulfur species adsorbed on PM

XAFS analyses of the sulfur K-edge spectra were performed using the BL11 at the

Hiroshima Synchrotron Research Center (HiSOR). Synchrotron radiation from a bending magnet was monochromatized with a Si (111) double-crystal monochromator. The sample chamber was filled with He gas. The XAFS spectra were measured in two different modes simultaneously. The X-ray fluorescence yield using XR-100FAST SDD (Amptekas) mounted on double-sided tape (NW-K15; Nichiban) and placed in the central hole (15 mm in diameter) of a copper plate. The angle between the incident X-rays and the sample surface was 20 degrees. X-ray fluorescence was detected from the directias mounted on double-sided tape (NW-K15; Nichiban) and placed in the central hole (15 mm in diameter) of a copper plate. The angle between the incident X-rays and the sample surface was 20 degrees. X-ray fluorescence was detected from the direction normal to the incident beam in the plane of the electron orbit of the storage ring. The X-ray window of the detector (C1 model) utilizes silicon nitride (Si_3N_4) with an aluminum coating to extend the low-energy response down to carbon.

The references; $Na_2S_2O_8$, $FeSO_4 \cdot 7H_2O$, sodium lauryl sulfate, sodium p-toluene sulfonate, $Na_2S_2O_3$, Na_2SO_3, and $(CH_3)_2SO$ (all from Wako Pure Chemical Industry); DMX (distillate marine fuel); engine oil (15W-40: Yanmar); dibenzothiophen, tert-thiophene, L-methionine, di-t-butyl disulfide, and elemental sulfur (all from Wako Pure Chemical Industry); FeS_2 (Stream Chemicals); and FeS (Wako Pure Chemical Industry)

were measured using both the conversion electron yield mode and X-ray fluorescence yield mode simultaneously.

Total sulfur concentration in PM was measured by an Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES Optima7300 DV; Perkin Elmer). Prior to ICP-AES analyses, approximately 0.2 g of filter with PM samples was digested by a mixed acid (HCl 0.3 mL, HNO_3 4mL and HBF_4 1 mL) under 230 ^oC for 30 min in a microwave digestion system (MWS-3; Actac).

3. Results and discussion

3.1 Effect of sulfur content in fuel on sulfur species adsorbed on PM

The four-stroke diesel engine was operated with DMX and sulfur-added fuel. **Figure S2** shows concentration of PM in exhaust gas and sulfur adsorbed under operations using fuel with different sulfur content. PM concentration in exhaust gas using the DMX (sulfur content: 0.08%), 3.5, or 5% sulfur-added DMX was 145, 166 and 175 mg m^{-3}, respectively. The concentration of total sulfur adsorbed on PM was 28.4, 35.1 and 39.9 mg m^{-3}, respectively **(Fig. S2)**. PM concentration under 3.5 or 5% sulfur-added DMX operation was thus significantly higher than that of DMX ($p<0.01$-0.05). The concentration of total sulfur adsorbed on PM under 5% of sulfur-added fuel operation was also statistically high

199 compared to other fuel operations ($p<0.05$). The weight percentage of sulfur adsorbed on
200 PM ranged from 19.6–22.8%, and did not show statistical difference between sulfur
201 content in fuels. In contrast, SO_2 concentrations in exhaust gas were 12, 771 and 1150
202 ppm for DMX (sulfur content: 0.08%), 3.5%, and 5% of sulfur-added DMX operations,
203 respectively. SO_2 concentration increased linearly with sulfur content in fuels ($p<0.01$),
204 indicating that most of sulfur added to DMX was emitted as SO_2 gas (**Fig. S3**).

205 The sulfur K-edge spectra of PM and sulfur references are shown in **Figs. S4 and S5**.
206 Two peaks were observed at around 2482 eV and 2480.5 eV, representing sulfate and
207 sulfonate, respectively (**Fig. S4**). The sulfur K-edge spectra of PM fit well with the
208 combination of sulfate and sulfonate by the linear combination fit. We considered the
209 sulfate to be derived from the oxidation of sulfur substances in DMX and di-t-butyl
210 disulfide (sulfur added to DMX). The sulfonate might have been derived from DMX,
211 because sulfonate is one of the major components in sulfur species in petroleum (Waldo
212 et al., 1991), or from the oxidation of sulfide in DMX and di-t-butyl disulfide.

213 The concentration of sulfate adsorbed on PM under operation with 0.08, 3.5 and 5% of
214 sulfur-added DMX was 10.6, 21.5 and 27.0 mg m^{-3}, respectively, on the basis of amount
215 of sulfur (**Fig. S6**). The concentration of sulfate adsorbed on PM under operation with 3.5
216 and 5% of sulfur-added DMX was significantly higher compared to DMX ($p<0.01$).

There was a positive correlation between sulfur content in fuel and the concentration of sulfate adsorbed on PM (**Fig. 1**). In contrast, there was no statistically significant difference in concentration of sulfonate adsorbed on PM between the three fuels. Sulfonate concentration ranged from 12.9–17.9 mg m^{-3} on the basis of sulfur. Hence, sulfur added to DMX was considered to be mainly oxidized to sulfate and SO_2 gas (**Fig. S3 and Fig. 1**).

3.2 Sulfur species adsorbed on PM collected from seagoing ships

3.2.1 The container carrier, EMERALD I

PM samples were collected under navigation with 85% and 50% load; PM concentration in exhaust gas under navigation with these loads was 54.0 and 42.7 mg m^{-3}, respectively (**Fig. 2a**). Although the difference between 85% and 50% load was not statistically significant, PM concentration tended to be lower with the 50% load. These results were consistent with the findings of a previous study that PM total mass in exhaust gas was greater at light and high loads compared to middle loads (Chen et al., 2007). This was attributed to specific fuel consumption increase under light and high loads. The concentration of total sulfur-adsorbed PM was almost the same for the 85 and 50% load, 20.4 and 21.2 mg m^{-3}, respectively (**Fig. 2a**). This result appeared to be due to use of the

235 same sulfur content of DMX for both engine loads, a percent composition equivalent to
236 38 and 52% to the PM mass, respectively.

237 The sulfur K-edge spectra of PM collected from the EMERALD I and sulfur and
238 sulfonate standards are shown in **Fig. S7**. The sulfur K-edge spectra of the PM fit well
239 with the combination of sulfate and sulfonate by the linear combination fit. The origin of
240 sulfate and sulfonate in PM is considered to be the oxidation of sulfur substances and
241 sulfide in DMX. The concentration of sulfate and sulfonate adsorbed on PM under 85%
242 load were 19.0 and 1.3 mg m^{-3}, respectively, on the sulfur basis (**Fig. 2b**). In the case of
243 50% load, concentration of sulfate and sulfonate adsorbed on PM were 20.2 and 1.0 mg
244 m^{-3}, respectively, on the sulfur basis (**Fig. 2b**). The sulfur species of PM did not show a
245 statistically significant difference between 85% and 50% load.

246

247 **3.2.2 The training vessel, FUKAE-MARU**

248 PM samples were collected under navigation with 94% and 70% load. The PM
249 concentration in exhaust gas under these loads was 83.4 and 59.5 mg m^{-3}, respectively
250 **(Fig. 3a)**. PM concentration was lower under 70% load than under 94% ($p<0.05$). The
251 concentration of total sulfur adsorbed PM was almost the same for the 94 and 70% load,
252 12.5 and 11.5 mg m^{-3}, a percent composition equivalent to 15 and 19% of PM mass,

253 respectively **(Fig. 3a)**. The sulfur content of DMX used by the FUKAE-MARU (0.062%)
254 was less than that of the EMERALD I (0.78%), resulting in a 39–46% lower concentration
255 of total sulfur adsorbed PM in exhaust gas.

256 The sulfur K-edge spectra of PM collected from the FUKAE-MARU is shown in **Fig.**
257 **S8**, together with the sulfur, sulfite and sulfonate standards. The sulfur K-edge spectra of
258 the PM fit well with the combination of sulfate, sulfite and sulfonate by the linear
259 combination fit. These sulfur species are considered to result from the oxidation of sulfur
260 substances in DMX. The concentration of sulfate, sulfite and sulfonate adsorbed on PM
261 under 94% load was 8.3, 2.6, and 1.5 mg-S m^{-3}, respectively, on the sulfur basis (**Fig. 3b**).
262 In the case of 70% load, concentration of adsorbed sulfate, sulfite and sulfonate was 9.0,
263 1.1, and 1.5 mg-S m^{-3}, respectively, on the sulfur basis. The difference in sulfur species
264 adsorbed on PM between 94 and 70% loads was not significantly different. The results
265 obtained for the FUKAE-MARU were in good agreement with those of the EMERALD
266 I. Similarly, in terms of the concentration of total sulfur adsorbed on PM, the FUKAE-
267 MARU was 55–56% less than that of the EMERALD I.

268

269 **3.2.3 Sulfur species in soot collected from ship funnels**

270 The total sulfur concentration in soot increased with increasing fuel sulfur content (**Fig.**

271 **4**). The total sulfur concentration in soot from the HIROSHIMA-MARU (0.4%) was
272 significantly low compared to other vessels (3.0–9.8%; **Fig. 4**). This might have been due
273 to the use of gas oil, in which sulfur content is much lower (0.0006%) than that of DMX
274 (0.062-0.85%). The FUKAE-MARU, operated using low-sulfur DMX (0.062%), was the
275 second lowest in terms of sulfur content in soot. The low sulfur content in the DMX could
276 be the source of its low sulfur emissions. In the case of the TOYOSHIO-MARU,
277 EMERALD I, and KASUGA-MARU II, the ships were operated using DMX with similar
278 sulfur content (0.79–0.85%) and produced similar sulfur concentration in soot (7.4–9.8%).
279 **Figure S9** shows the sulfur K-edge spectra of soot samples, and sulfate, sulfonate,
280 thiophene and DMX. Similarly, peaks representing sulfate and sulfonate derived from
281 fuel or sulfur oxidation in DMX were observed, and the broad peak was identified around
282 2471-2475 eV, except in the HIROHIMA-MARU. Because the major sulfur species in
283 petroleum are sulfide, thiophene and sulfoxide (Waldo et al., 1991), we tried to fit the
284 broad peak using these references. The broad peak at 2471-2475 eV was in good
285 agreement with X-ray absorption energy of DMX, thiophene, and engine oil (**Figs. S9**
286 **and Fig. S5**), indicating that the broad peak originated from sulfur compounds such as
287 exocyclic sulfur, heterocyclic sulfur, and disulfide in DMX and engine oil (Waldo et al.,
288 1991; Kittelson 1998; Manceau and Nagy 2012). The sulfur K-edge spectra of the soot

289 fit well with the combination of sulfate, sulfonate, thiophene and DMX by the linear
290 combination fit (**Fig. S9**).

291 The sulfur species of soot collected from the HIROSHIMA-MARU and FUKAE-
292 MARU, which were operated by gas oil (sulfur content: 0.0006%) and low-sulfur DMX
293 (0.062%) was mainly composed of sulfate; concentrations in soot were 4.0 and 25.8 mg
294 g^{-1} on the basis of sulfur, a percent composition equivalent to 100 and 87% of PM mass,
295 respectively (**Fig. 5**). In the case of the other ships operated using DMX (sulfur content:
296 0.79–0.85%), concentration of sulfonate, thiophene and organosulfur compounds
297 originating from DMX were significantly high compared to the HIROSHIMA-MARU
298 and FUKAE-MARU. The sulfate concentration in soot increased with increasing fuel
299 sulfur content (**Fig. 6**). In contrast, there was no clear relationship between the sulfur
300 content of fuel and concentration of the other sulfur species in soot. However, the
301 organosulfur tended to increase with increasing sulfur content in fuels. These
302 organosulfur compounds derive from incomplete combustion of the carbonaceous
303 components in fuel (Huggins and Huffman, 2002). Therefore, it was considered the
304 organosulfur concentration in soot was well correlated with the operating conditions of
305 the engine of each vessel rather than with the sulfur content of the fuel.

306

Conclusions

This is the first study to investigate the composition of sulfur species adsorbed on PM in various ship exhaust gases. The concentration of total sulfur in PM, and of sulfate adsorbed on PM from the ship exhaust gas, increased with increasing fuel sulfur content. However, in contrast to previous studies, although PM concentration under high load was greater than under middle load, the sulfur concentration adsorbed on PM and sulfur species did not differ between high and middle loads. Therefore, this study confirmed that the regulation of sulfur content in fuels is an e□ective strategy for reducing sulfate in PM and soot emitted from seagoing ships. In addition to sulfate, we newly identified sulfonate derived from fuel or oxidation of sulfide in fuel. Current regulations might be not e□ective in reducing sulfonate because concentration of sulfonate wad not necessarily dependent on the sulfur content of fuel. Furthermore, radiative forcing of PM emitted from seagoing ships may also change depending on the species of sulfur.

In the case of soot, total sulfur and sulfate concentrations increased with increasing fuel sulfur content. The concentration of organosulfur in soot, such as thiophen and sulfonate, originating mainly from DMX and engine oil, tended to increase as sulfur content in fuels increased. These organosulfur compounds derive from incomplete combustion of the carbonaceous components in the fuel. Therefore, organosulfur compounds would not be

reduced simply by regulating the sulfur content of fuel.

Acknowledgements

The authors would like to thank Koji SEIDA, Toshifumi CHAEN and the crew members of the HIROSHIMA-MARU, National Institute of Technology, Hiroshima College, and Shiro KOBAYASHI and the crew members of the KASUGA-MARU II, Maruei Co., Ltd. for their help with sampling and thoughtful suggestions.

The authors are grateful to Yoshiji YANO, Yoshiharu ITAMI and the crew members of the FUKAE-MARU, Kobe University, Kadumitsu NAGAGUCHI, Mitsuru KUBOTA and the crew members of the TOYOSHIO-MARU, Hiroshima University, and Takeharu OHNISHI and the crew members of the EMERALD I, Aoki Marine Co., Ltd. for their help with sampling and navigation.

XAFS analyses at the Hiroshima Synchrotron Radiation Center, Hiroshima University, were carried out under the approval of the Project for Collaborative Research (13-A-3, 17BG011).

We express our gratitude to Hideki TANAKA, Kenya HIROSAWA, Wataru HIRAOKA, and Toru HAYAKAWA, students at the graduate school of maritime sciences, Kobe University, for their support during the sampling.

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344 **References**

345 Agrawal, H., Welch, W.A., Miller, J.W., Cocker, D.R. 2008a. Emission measurements
346 from a crude oil tanker at sea. Environ. Sci. Technol., 42, 7098-7103, DOI
347 10.1021/es703102y

348 Agrawal, H., Malloy, Q.G.J., Welch, W.A., Miller, J.W., Cocker III, D.R. 2008b. In-use
349 gaseous and particulate matter emissions from a modern ocean going container
350 vessel. Atmos. Environ., 42, 5504-5510, DOI 10.1016/j.atmosenv.2008.02.053

351 Alfoldy, B., Loov, J.B., Lagler, F., Mellqvist, J., Berg, N., Beecken, Weststrate, H.,
352 Duyzer, J., Bencs, L., Horemans, B., Cavalli, F., Putaud, J.P., Janssens-Maenhout,
353 G., Csordas, A.P., Van Grieken, R., Borowiak, A., Hjorth, J. 2013. Measurements of
354 air pollution emission factors for marine transportation in SECA. Atmos. Meas.
355 Tech., 6, 1777-1791, DOI 10.5194/amt-6-1777-2013

356 Berechman, J., Tseng, P.H. 2012. Estimating the environmental costs of port related
357 emissions: The case of Kaohsiung. Transport. Res. Part D: Transport and Environ.,
358 17, 35-38, DOI 10.1016/j.trd.2011.09.009

359 Capaldo, K, Corbett, J.J., Kasibhatla, P., Fischbeck, P., Pandis, S.N. 1999. Effects of ship
360 emissions on sulphur cycling and radiative climate forcing over the ocean. Nature,

400, 743-746, DOI 10.1038/23438

Chen, H., Shuai, S.J., Wang, J.X. 2007. Study on combustion characteristics and PM emission of diesel engines using ester-ethanol-diesel blended fuels. Proc. Combust. Inst. 31, 2981–2989, DOI 10.1016/j.proci.2006.07.130

Doney, S.C., Mahowald, N., Lima, I., Feely, R.A., Mackenzie, F.T., Lamarque, J.F., Rasch, P.J. 2007. Impact of anthropogenic atmospheric nitrogen and sulfur deposition on ocean acidification and the inorganic carbon system. PNAS 104, 14580-14585, DOI 10.1073/pnas.0702218104

Endres, S., Maes, F., Hopkins, F., Houghton, K., Mårtensson, E.M., Oeffner, J., Quack, B., Singh, P., Turner, D. 2018. A new perspective at the ship-air-sea-interface: The environmental impacts of exhaust gas scrubber discharge. Front. Mar. Sci., 5, 139, DOI 10.3389/fmars.2018.00139

Endresen, Ø., Bakke, J., Sørgård, E., Berglen, T. Flatlandsmo, Holmvang, P. 2005. Improved modelling of ship SO_2 emissions—a fuel-based approach. Atom. Environ. 39, 3621-3628, DOI 10.1016/j.atmosenv.2005.02.041

Huggins, F.E, Huffman, G.P. 2002. X-ray absorption fine structure (XAFS) spectroscopic characterization of emission from combustion of fossil fuels. Int. J. Soc. Mater. Eng. Res. 10, 1-13, DOI 10.5188/ijsmer.10.1

379 Huggins, F.E., Shah, N., Huffman, G.P., Robertson, J.D. 2000. XAFS spectroscopic
380 characterization of elements in combustion ash and fine particulate matter. Fuel
381 Process. Thechnol. 65-66, 203-218, DOI 10.1016/S0378-3820(99)00089-2
382 Kittelson, D.B. 1998. Engines and nanoparticles: a review. J. Aerosol Sci. 29, 575-588,
383 DOI 10.1016/S0021-8502(97)10037-4
384 Lützenkirchen-Hecht, D., Müller, L., Hoffmann, L., Wagner, R. 2014. Analyses of
385 engine motor oils by X ray absorption and X-ray fluorescence spectroscopies. X-
386 Ray Spectr. 43, 221-227, DOI 10.1002/xrs.2543
387 Manceau, A., Nagy, K.L. 2012. Quantitative analysis of sulfur functional groups in
388 natural organic matter by XANES spectroscopy. Geochim. Cosmochim. Ac. 99,
389 206-223, DOI 10.1016/j.gca.2012.09.033
390 Moldanová, J., Fridell, E., Popovicheva, O., Demirdjian, B., Tishkova, V., Faccinetto,
391 A., Focsa, C. 2009. Characterization of particulate matter and gaseous emissions
392 from a large ship diesel engine. Atmos. Environ. 43, 2632-2641, DOI
393 10.1016/j.atmosenv.2009.02.008
394 Mölders, N., Schilling, P.J., Wong, J., Roos, J.W., Smith, I.L. 2001. X-ray fluorescence
395 mapping and micro-XANES spectroscopic characterization of exhaust particulates
396 emitted from auto engines burning MMT-added gasoline. Environ. Sci. Technol.,

35, 3122-3129, DOI 10.1021/es0010958

Mousavi, A., Sowlat, M.H., Hasheminassab, S., Pikelnaya, O., Polidori, A., Ban-Weiss, G., Sioutas, C. 2018. Impact of particulate matter (PM) emissions from ships, locomotives, and freeways in the communities near the ports of Los Angeles (POLA) and Long Beach (POLB) on the air quality in the Los Angeles county. Atmos. Environ., 195, 159-169, DOI 10.1016/j.atmosenv.2018.09.044

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

Ostro, B., Tobias, A., Querol, X., Alastuey, A., Amato, F., Pey, J., Pérez, N. Sunyer, J. 2011. The effects of particulate matter sources on daily mortality: A case-crossover study of Barcelona, Spain. Environ. Health Pers., 119, 1781-1787, DOI 10.1289/ehp.1103618

Querol, X., Alastuey, A., Rodriguez, S., Plana, F., Ruiz, C.R., Cots, N., Massagué, G., Puig, O. 2001. PM10 and PM2.5 source apportionment in the Barcelona metropolitan area, Catalonia, Spain. Atmos. Environ., 35., 6407-6419, DOI

10.1016/S1352-2310(01)00361-2

Schröder, C., Reimer, N., Jochmann, P. 2017. Environmental impact of exhaust emissions by Arctic shipping. Ambio 46, 400-409, DOI 10.1007/s13280-017-0956-0

Smith, T.W.P., Jalkanen, J.P., Anderson, B.A., Corbett, J.J., Faber, J., Hanayama, S., O'Keeffe, E., Parker, S., Johansson, L., Aldous, L., Raucci, C., Traut, M., Ettinger, S., Nelissen, D., Lee, D.S., Ng, S., Agrawal, A., Winebrake, J.J., Hoen, M., Chesworth, S., Pandey, A. 2015. Third IMO GHG Study 2014. 291pp, London.

Tzannatos, E. 2010. Ship emissions and their externalities for the port of Piraeus- Greece. Atom. Environ. 44, 400-407, DOI 10.1016/j.atmosenv.2009.10.024

Waldo, G.S., Carlson, R.M.K., Moldowan, J.M., Peters, K.E., Penner-Hahn, J.E. 1991. Sulfur speciation in heavy petroleums: Information from X-ray absorption near-edge structure. Geochim. Cosmochim. Ac. 55, 801-814, DOI 10.1016/0016-7037(91)90343-4

Highlights

- Sulfur species adsorbed on PM in ship exhaust gas were identified.
- The sulfur species of PM did not change between high and middle loads.
- Sulfate, sulfite, sulfonate, and thiophen were identified in PM and soot.
- Sulfonate was derived from fuel or oxidation of sulfide in fuel.
- Sulfate in soot increased with increasing sulfur content in fuels.

Figures

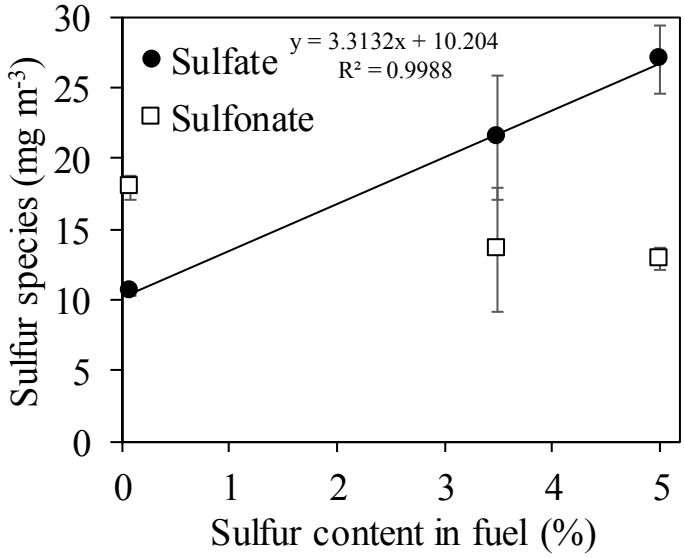

Fig. 1 Relationship between concentration of sulfate adsorbed on PM and sulfur content in fuels

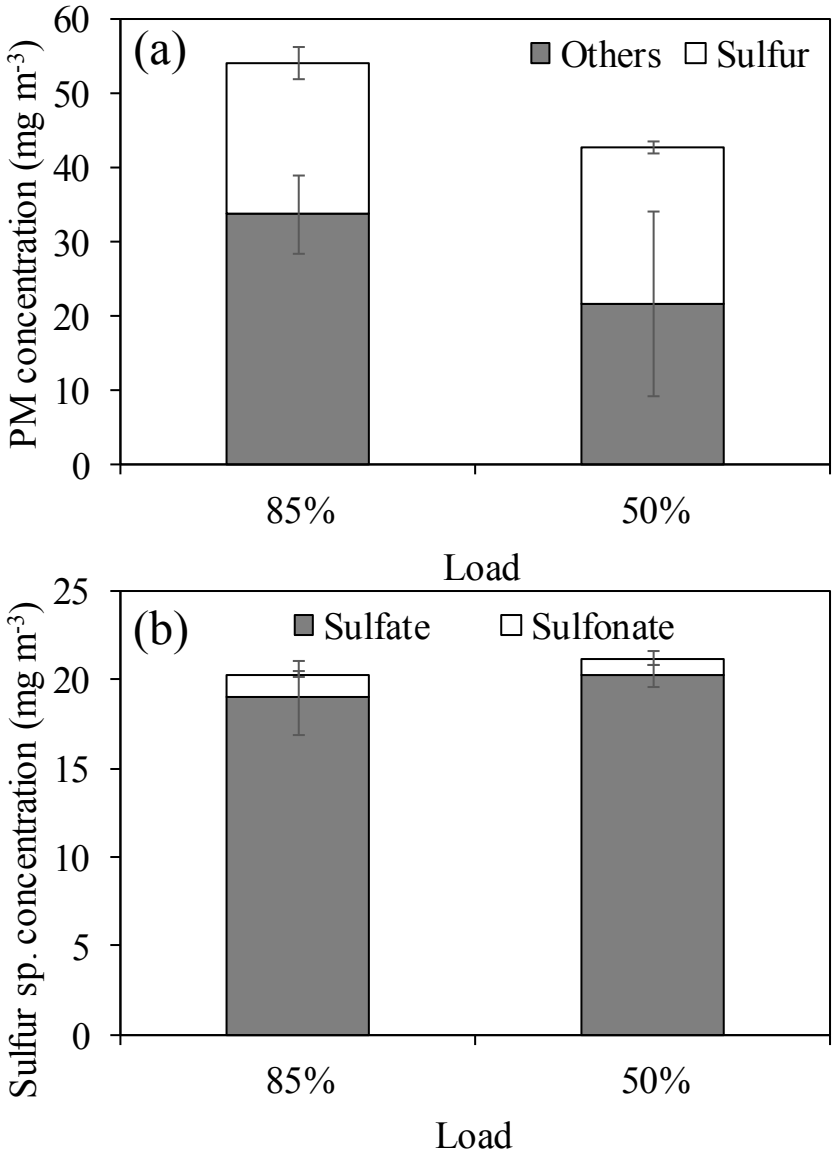

Fig. 2 PM and sulfur concentartions (a) and concentrations of sulfate and sulfonate (b) adsorbed on the PM emitted from EMERALD I

Error bars are standard deviation.

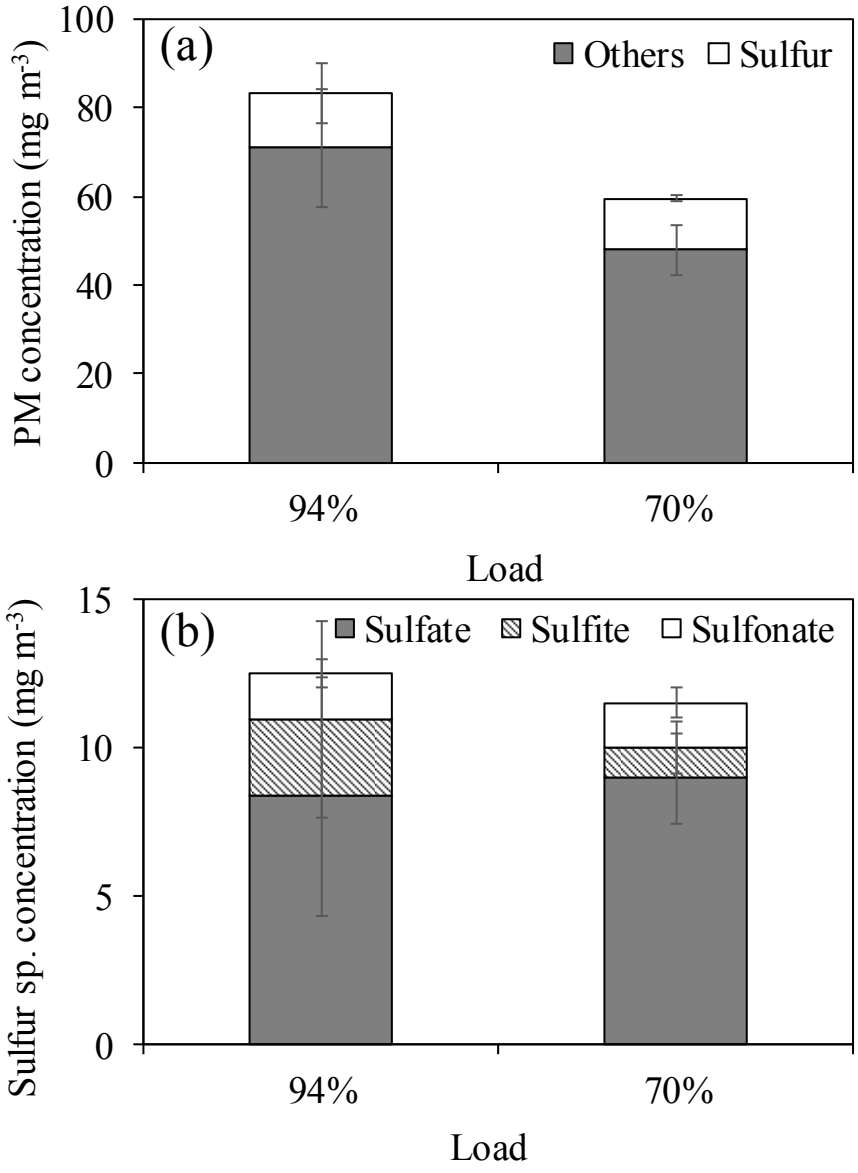

Fig. 3 PM and sulfur concentrations (a) and concentrations of sulfate, sulfite and sulfonate (b) adsorbed on the PM emitted from FUKAE-MARU

Error bars are standard deviation.

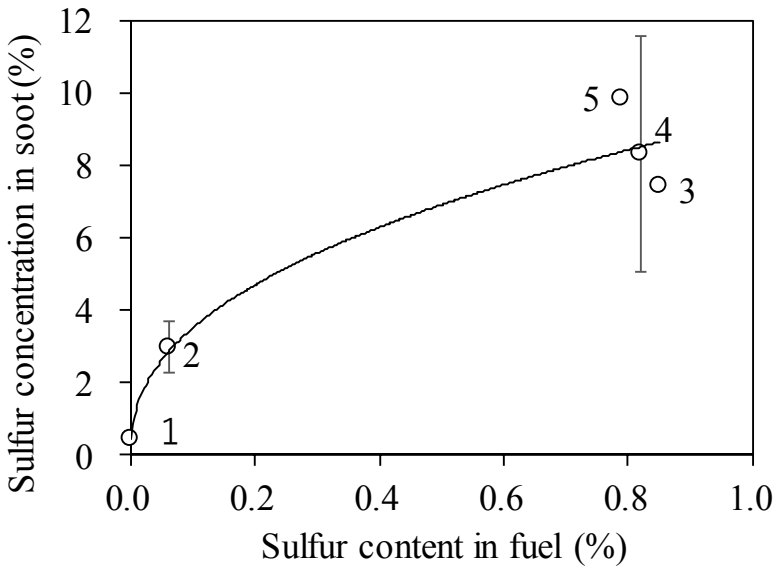

Fig. 4 Relationship between sulfur content in fuel and sulfur concentration in soot collected from each vessel

1) HIROSHIMA-MARU (Spot sampling); 2) FUKAE-MARU; 3) KASUGA-MARU II (Spot sampling); 4.) TOYOSHIO-MARU; and 5) EMERALD I (Spot sampling).

Error bars indicate standard deviation of the FUKAE-MARU (No. 2) and TOYOSHIO-MARU (No. 4)

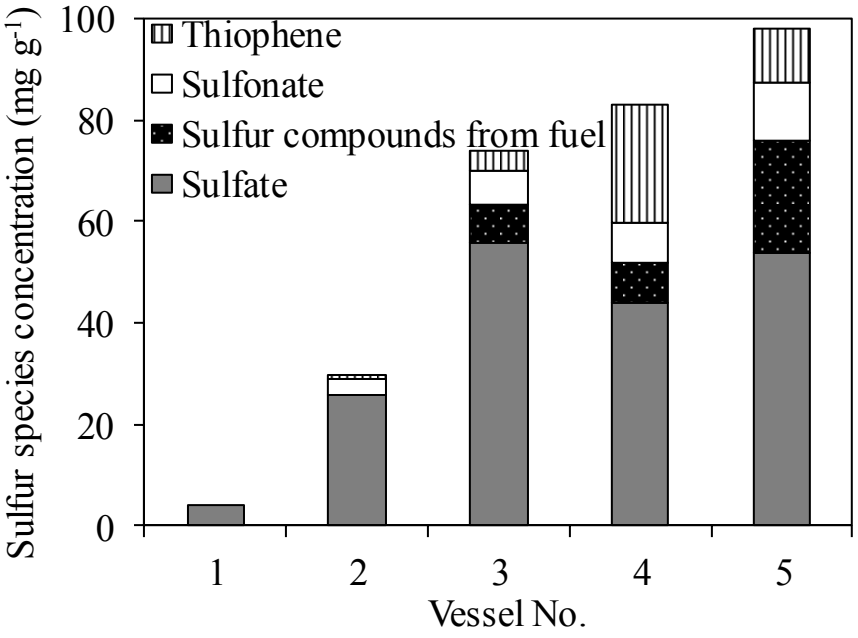

Fig. 5 Concentrations of sulfur species in soot collected from each vessel

1. HIROSHIMA-MARU; 2. FUKAE-MARU; 3. KASUGA-MARU II; 4. TOYOSHIO-MARU; 5. EMERALD I

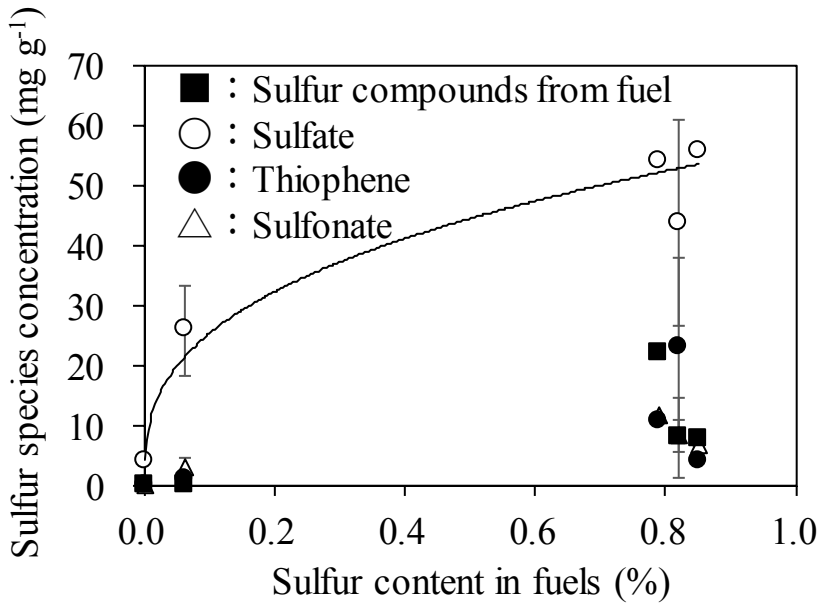

Fig. 6 Relationship between sulfur content in fuel and concentrations of sulfur species in soot collected from each ship

Error bars indicate standard deviation of the FUKAE-MARU and TOYOSHIO-MARU.

Table 1 Vessels used in this study to collect PM or soot samples

Vessel name	Vessel Type	Tonnage (t)	Engine	Rated output (kW)	Fuel	Sulfur content in fuel (%)
EMERALD I	Container carrier	5215 (DWT)	6DKM-26L (DAIHATSU)	1470 x 2	DMX	0.79
KASUGA-MARU II	Tugboat	19(GT)	6MG22X (NIIGATA ENGINEERING)	810	DMX	0.85
TOYOSHIO-MARU	Research and Training	256(GT)	6NY16L-EN (YANMER)	441 x 3	DMX	0.82
HIROSHIMA-MARU	Training	769(GT)	6N260L-UN (YANMER)	956	Gas oil	0.0006
FUKAE-MARU	Training	449(GT)	6DKM-26S (DAIHATSU)	1100	DMX	0.062

Supplemental materials

Identifying sulfur species adsorbed on particulate matters in exhaust gas emitted from various vessels

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EMERALD I

KASUGA-MARU II

TOYOSHIO-MARU

HIROSHIMA-MARU

FUKAE-MARU

Fig. S1 Vessels used in this study to collect PM and soot samples

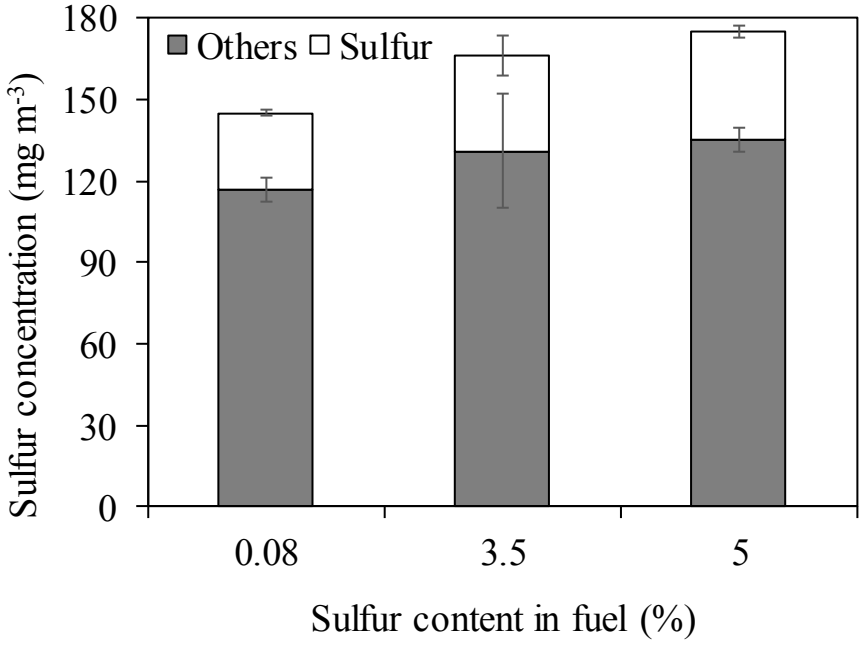

Fig. S2 PM concentration and sulfur concentration adsorbed on the PM under operation with different sulfur content in fuels

Error bars are standard deviation.

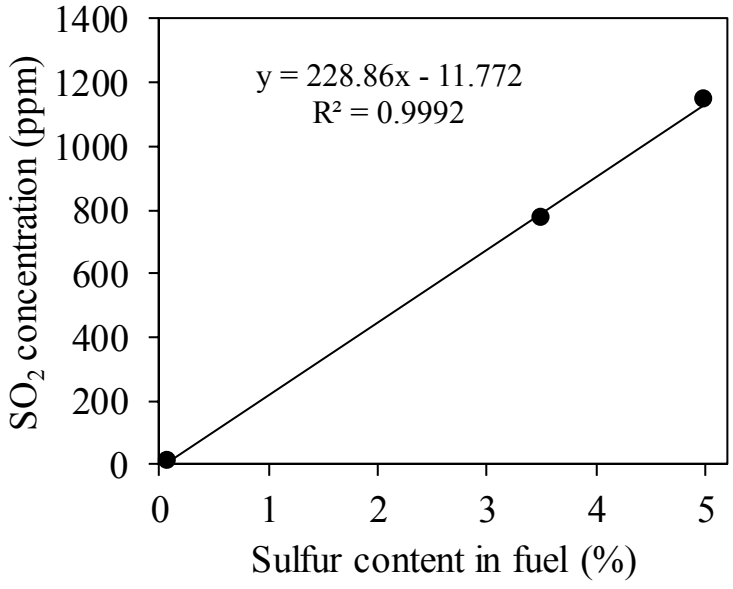

Fig. S3 Relationship between SO_2 concentration in exhaust gas and sulfur content in fuels

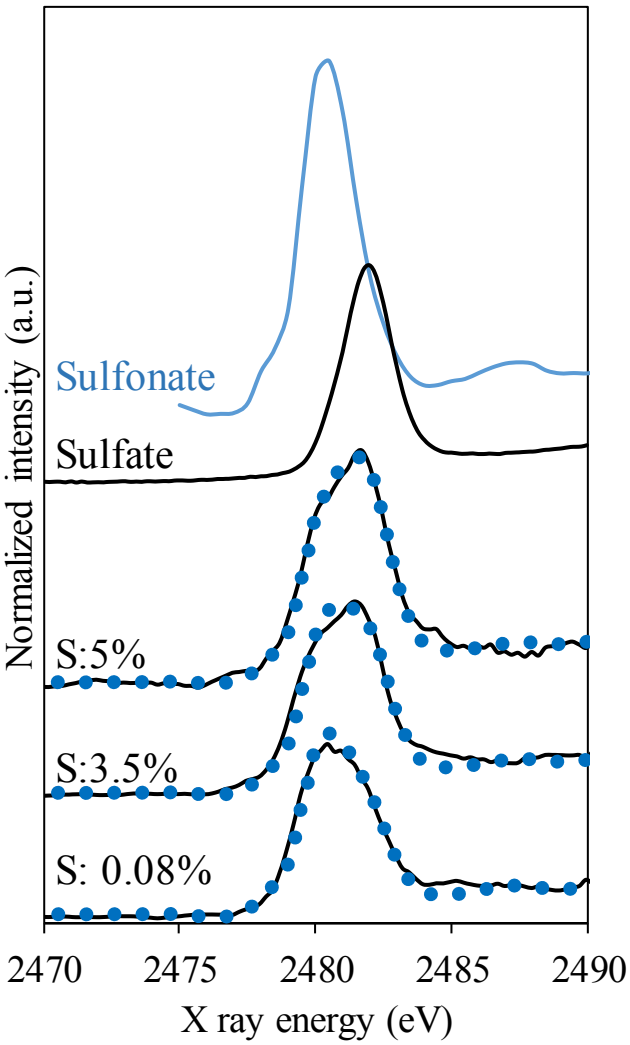

Fig. S4 Sulfur K edge spectra of PM from diesel engine under operation with different sulfur content (0.08-5%) in fuel

Dotted lines are liner combination fit by the two standards.

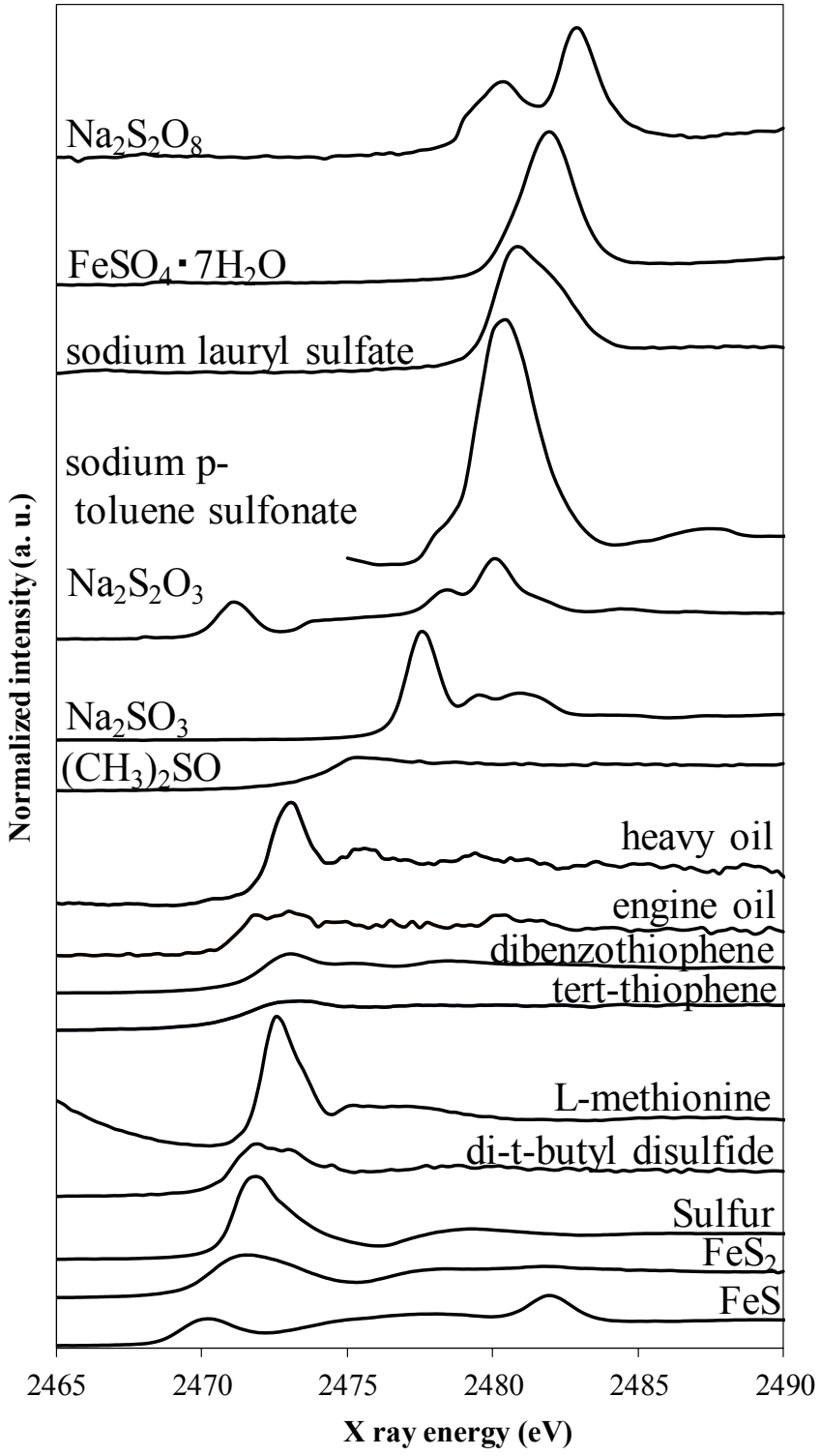

Fig. S5 Sulfur K edge spectra of sulfur references

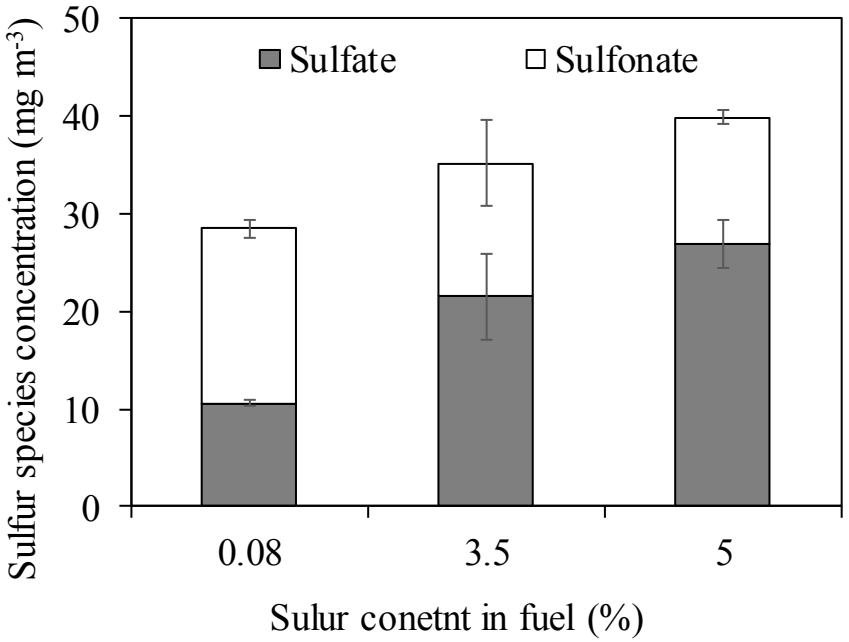

Fig. S6 Sulfur and sulfonate concentrations adsorbed on the PM emitted from diesel engine under operation with different sulfur content (0.08-5%) in fuel

Error bars are standard deviation.

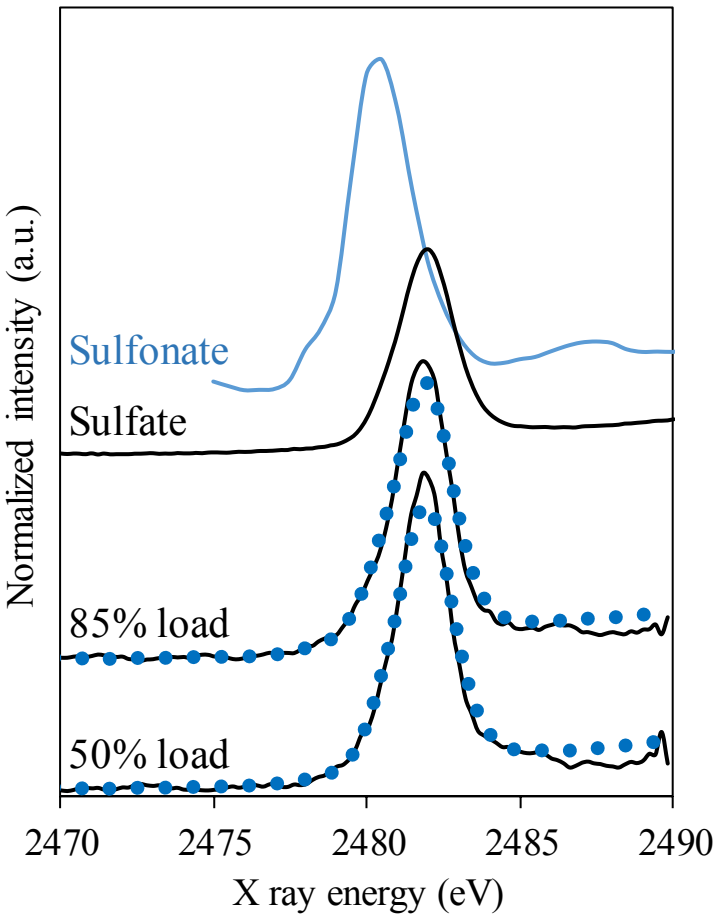

Fig. S7 Sulfur K edge spectra of PM from EMERALD I and sulfate standards
Dotted lines are liner combination fit by the two standards.

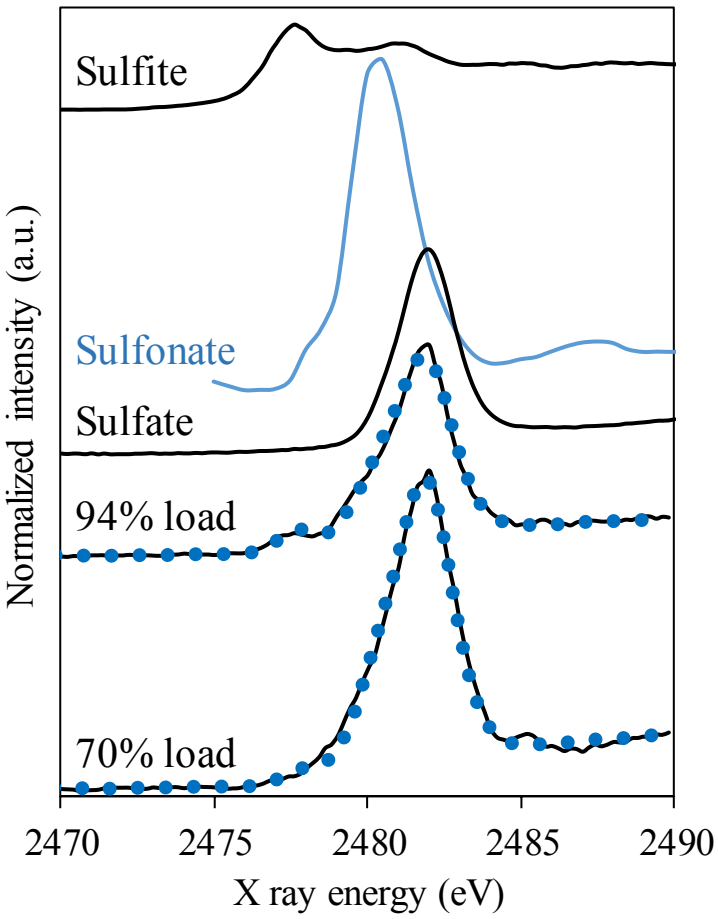

Fig. S8 Sulfur K edge spectra of PM from FUKAE-MARU, sulfonate and sulfate standards

Dotted lines are liner combination fit by the two standards.

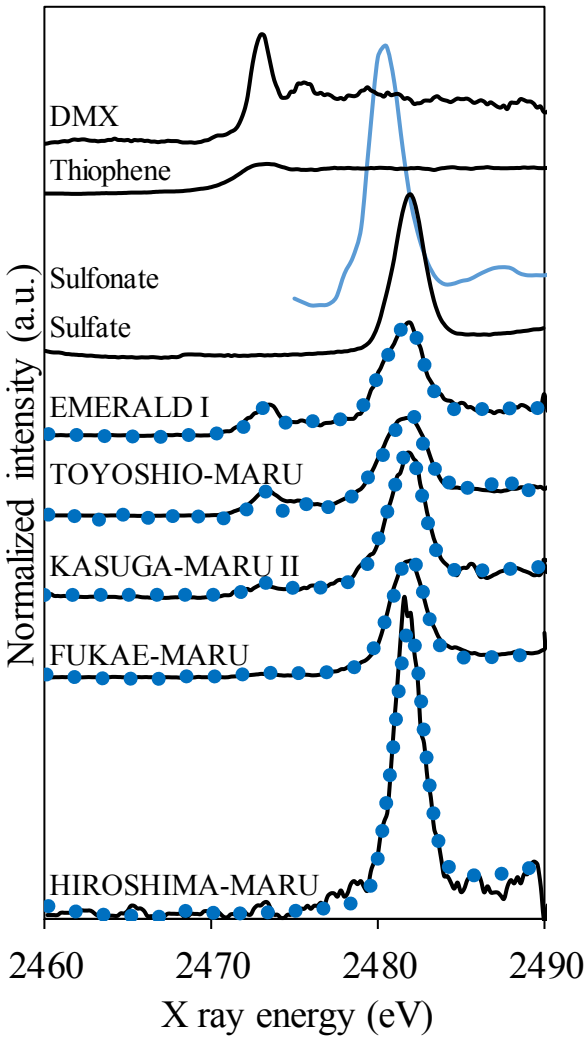

Fig. S9 Sulfur K edge spectra of soot collected from each ship and several sulfur standards

Dotted lines are liner combination fit by the two standards.