Response to Referee's Comments #2

1. The ratio SO_2/NO_X in order to determine whether a ship uses heavy fuel oil or distillate oil needs more discussion. NO_X-emissions are mainly related to engine and combustion characteristics. My question is why not use SO_2/CO_2 ratio?

Response:

Thanks for your suggestion. We agree that the SO_2/CO_2 ratio of ship plume is a better indicator of fuel sulfur content than the SO_2/NO_x ratio, and is widely used in several in site measurements (Kattner et al., 2015; Loov et al., 2014; Yang et al., 2016). However, we are aware of that in China, the concentration of CO_2 is excluded from ambient air measurement. The Ambient Air Quality Standards (China National Standard GB 3095-2012) stipulates the monitoring of six pollutants in ambient air, which is SO_2, NO_2 (or NO_x), O_3, CO, $PM_{2.5}$ and PM_{10}. Hence, the CO_2 measurement is not equipped on from thousands of micro-monitor stations to medium or even mobile monitor stations. To use monitoring capacity maximumly, we would like to explore a relatively reliable and practical indicator within the six pollutants mentioned above. According to the Third IMO GHG Study, NO_x emissions do vary by engine and combustion. But based on the ship information provided by JT, the size of berth and the design of port, we found ships in JT, especially those related to identified plumes, mainly consistent in size. Actually, ship information provided by the port during campaign indicates the variance of ship size is little in Jingtang Harbor. All these conditions make the SO_2/NO_x ratio reliable and convincing for indicating fuel sulfur content in Jingtang Harbor. We believe it would be more appropriate to use SO_2/CO_2 ratio, but with the absence of CO_2 concentration and the consistency of ship size, the ratio SO_2/NO_x is also applicable.

Revision in manuscript:

1) *Page 6, Line 12-15: The SO_2 to CO_2 ratio in ship plume is widely used as an indicator for S_F (Yang et al., 2016; Kattner et al., 2015; Loov et al., 2014). However, in this study we intend to explore another applicable indicator for situation in China that the concentration of CO_2 is often excluded from ambient air measurement after the Ambient Air Quality Standards (China National Standard GB 3095-2012) stipulates the six pollutants to monitor without CO_2.*

2) *Page 6, Line 17-20: Moreover, based on the ship information provided by JT, the size of berth and the design of port, we found ships in JT, especially those related to identified plumes, mainly consistent in size, which implies similar NO_x emissions in those plumes (IMO, 2015). Therefore the NO_x to SO_2 ratio is appropriate to indicate the SF of ships in JT.*

2. Rather specify sea areas than refer to emissions from ships in Europe, (page 2, row 6) and if

possible consider multiple references to the emission estimates. Similar comment to statement on row 14 on ship emissions in eastern China.

Response:

Thanks for your suggestion. We tried to describe the impact of ship emissions in Europe and eastern China to lay a background for their corresponding ship emission regulation. And we agree with you that the statement was a little vague about sea areas and that our statement needs more references. So we specify the sea areas and summarize some valuable works as revision below.

Revision in manuscript:

1) *Page 2, Line 6-11: In the EU-27, ships in 2005 emitted 2.8 million tons NO_x, 1.7 million tons SO_2 and 0.2 million tons $PM_{2.5}$, of which approximately 70 % occurred within 200 nm from the coast of EU Member States (Campling et al., 2013). From 2006 to 2009, NO_x emission from ships rose by approximately 7 % in Baltic Sea, while SO_2 and $PM_{2.5}$ emissions reduced by 14 % and 20 %, respectively, mainly caused by the fuel requirements which became effective in 2006 (Jalkanen et al., 2014). In 2011, ship emission in Europe was estimated to be 2.0 million tons NO_x, 1.2 million tons SO_2 and 0.2 million tons $PM_{2.5}$ (Jalkanen et al., 2016).*
2) *Page 2, Line 18-22: Estimation of ship emissions within 200 nm to the Chinese coast showed that ship emissions accounted for an annual increase of up to 5.2 $\mu g \cdot m^{-3}$ $PM_{2.5}$ in eastern China, which influenced the air quality in not only coastal areas but also the inland areas hundreds of kilometers away from the sea (Lv et al., 2018). In 2010, ships contributed 12.0 % of SO_x, 9.0 % of NO_x and 5.3 % of $PM_{2.5}$ in total emission in Shanghai (Fu et al., 2012). And it was obtained that 14.1 % of SO_2, 11.6 % of NO_x and 3.6 % of $PM_{2.5}$ emission within the Pearl River Region, China in 2013, was attributed to ships (Li et al., 2016).*

3. Page 2 row 24, The NOX reductions should not be confused to be accomplished by the fuel switch.

Response:

Thanks for your suggestion. This paragraph was to present the expectation and effect of the fuel switch, and the NOx reductions mentioned here was confused just as you suggested. So we get rid of the NOx reductions in the manuscript.

Revision in manuscript:

Page 2, Line 32-33: Estimation shows that IMO limitation of 0.1% S_F in ECAs would reduce SO_2 emissions by 82 % by 2020 and further 23,000 tons of SO_2 by 2030 in European seas (Campling et al., 2013).

4. Page 4 row 10 on hourly measurements of $PM_{2.5}$ and PM_{10} by β-ray absorption should be explained. This is probably not the $\mu g/m^3$ measurements.

Response:

Thanks for your suggestion. According to the International Organization for Standardization, the β-ray absorption method is a method for the measurement of the mass of particulate matter in ambient air and is based on the absorption of beta rays by the particulate matter (ISO 10473:2000). The concentration was computed as follows:

$$C_{particles} = \frac{\Delta m \cdot S(Detection\ area, cm^2)}{q(sampling\ flow, m^3/h) \cdot t(sampling\ time, h)}$$

, where the mass per unit area of the particulate matter trapped in the filter

$$\Delta m(mg/cm^2) = \frac{\ln(N_1/N_2)}{k(absorption\ coefficient, cm^2/mg)}$$

The N_1 and N_2 represent the amount of β-ray passing through a blank filter and that trapped by particulate matter, respectively.

Similarly, several research describing the β-ray absorption method just as the equation above (Zhao et al., 2013; Zuo et al., 2017).

Revision in manuscript:

Page 4, Line 20-22: Monitoring modules consist of NO, NO_2 and NO_x measurement by an analyser, SO_2 detection by UV fluorometric, CO by IR absorption, O_3 by UV spectrophotometry, and particles by β-ray absorption (ISO 10473:2000).

5. Suggest to change "aerosol sample" to something like e.g. "exposed filter"

Response:

Thanks for your suggestion. We agree that “aerosol sample” is not as equally accurate as “exposed filter”. And we revise the manuscript as below.

Revision in manuscript:

1) Page 5, Line 1: 2.1.4 Particle samples

2) Page 5, Line 3-5: The filters were exposed for 23 h (normally from 16:30 to 15:30 LST the next day, local standard time, and named after the ending date) on an 80 mm-diameter pre-fired quartz microfiber filters (CHM QF1 grade) by a Laoying Model 2030 TSP sampler.

3) Page 5, Line 10-12: 0.55 cm^2 section of each exposed filter and blank filters were measured for concentrations of organic carbon (OC) and elemental carbon (EC) by the Thermal Optical Transmission Method in a DRI 2001 organic carbon/elemental carbon (OC/EC) analyser.

4) *Page 5, Line 19-20: 50 cm^2 section of each exposed filter and blank filters were extracted with 10 ml ultra-pure water in an ultrasonic bath at 4 ℃ for 30 min.*

5) *Page 5, Line 25-26: 20 cm^2 section of each exposed filter and blank filters were digested with 25 ml of an 8 %-HCl/ 3 %-HNO_3 solution in an ultrasonic bath at 69 ℃ for 3 h.*

6. Explain more on why only 16 plume events are identified - the period was long and the port is described as very busy.

Response:

Thanks for your suggestion. The port is busy indeed, but there are several reasons for the rather few plume event. Firstly, during our measurement, there was a period when ships barely went into the port due to the New Year holidays and also due to the poor visibility from January 1 to 4, 2017. Secondly, the wind direction in JT changes quickly, and sometimes it was unfavorable for instrument to capture the ship plume. And the prevailing wind direction indicates our plumes would be mainly from the 2nd pool and the 3rd pool, of which approximately half berth were actually in construction and not in use, making our plumes quite few. Thirdly, the port is actually quite polluted (in over 50 % of days, $PM_{2.5}$ concentration was above 115 $\mu g \cdot m^{-3}$), and the pollutants concentration can be rather high and may cover the existence of a ship plume event. So if the ship plume was emitted relatively far from the instrument, it would be difficult to distinguish the ship plume from background data even if the instrument captured the plume. Moreover, the measurement site is also in the vicinity of busy trucks which can be another interference. The manuscript is revised as below.

Revision in manuscript:

Page 6, Line 16-31: For these time stamps, peaks in NO_x along with simultaneous valleys in O_3 were then identified in valid data. The signals were only affirmed when there were significant peaks and clearly determinable backgrounds. Finally ship plume event were marked if the existence of ships was positive in the upwind direction of those signals. The combination of the trace gas peak time, the wind direction, and the ship traffic information (time of ships leaving and berthing) provided by marine administration in the port will enable the identification of the plume-related ship. For example, a ship plume event was identified in 5 January 2017 from 15:36 to 16:08 (Fig. 2). The timing and conditions associated with 16 positively identified ship plume event are listed in Table 1. Several situations made it more difficult to identify a ship plume event in our measurement. Firstly, there was a period when ships barely went into the port due to the New Year holidays and also due to the poor visibility from January 1 to 4, 2017. Secondly, the prevailing wind direction indicates our plumes would be mainly from the 2nd pool and the 3rd pool,

of which approximately half berth were actually in construction and not in use, making our plumes quite fewer than expect, let alone the fact that wind direction is actually changes quickly and sometimes unfavourable for instrument to capture the ship plume. Thirdly, the port is actually quite polluted (in over 50 % of days, $PM_{2.5}$ concentration was above 115 $\mu g \cdot m^{-3}$, see section 3.1.1), and the pollutants concentration can be rather high and may cover the existence of a ship plume event. Moreover, the measurement site is also in the vicinity of busy trucks which can be another interference.

7. Page 6 row 16. Suggest rewrite "In addition, high concentrations of organics, metals and the compounds between are obtained in IFOs from their presence in the original crude oil." This is an unclear statement.

Response:

Thanks for your suggestion. We agree with you that the statement is unclear and can be quite confusing. The manuscript is revised as below.

Revision in manuscript:

Page 7, Line 17-18: In addition, IFOs obtain high concentrations of organics, metals, and the compounds of organic metal from their presence in the original crude oil.

8. Page 6 on hybrid fuels: It is important to point out that these fuels can be anything from low sulphur heavy oils to qualities close to gasoils. The important issue is that there is no standard for these fuels (e.g. ISO-standard) and the only rquirement is that the sulphur is less than specified (<0.1%)

Response:

Thanks for your suggestion. We agree with you that the situation of hybrid fuels should be stated clearly and the previous description is quite vague. We revise the manuscript and point out the unsupervised situation of hybrid fuels.

Revision in manuscript:

Page 7, Line 31-Page 8, Line 3: Another record worth mentioning is that hybrid fuels that blend IFO and other low S_F fuels to comply with S_F limit are found widely used by ships operating in SECAs (Winnes et al., 2016; Zetterdahl et al., 2016), since the price of distillate fuels is an obstacle for contractors to completely abandon IFOs. However, by now ISO 8217:2017, the benchmark for the quality of marine fuels on the market, has not obtain any limits of physical and chemical parameters for hybrid fuels. It causes a large uncertainty of their qualities since there are zero formal standard for quality of hybrid fuels except the requirement of S_F.

9. Page 10 row 7. The OC/EC ratio in ship emissions is probably both dependent to fuel (residual or distillate) and to engine characteristics and therefore varies a lot.

Response:

Thanks for your suggestion. The OC/EC ratio is indeed under influence of both fuel and engine, but several emission factor studies suggest the fact that OC/EC emission ratio is strongly distinguishable between marine combustion (typically over 10) and on-road diesel engine (typically lower than 1) (Celo et al., 2015; Khan et al., 2012; Moldanová et al., 2009; Oanh et al., 2010; Sippula et al., 2014). Therefore, the higher value of OC/EC ratio of aerosols in JT may indicate the worse influence of ship emissions than other port city like Hong Kong. We revise the manuscript with a more appropriate expression as below.

Revision in manuscript:

Page 11, Line 6-10: Despite the OC/EC emission ratio dependent to both fuel type and engine, tests show that it is still strongly distinguishable between marine combustions (typically over 10) (Celo et al., 2015; Moldanová et al., 2009; Sippula et al., 2014) and on-road diesel engine (typically ranging from 0.25 to 1) (Oanh et al., 2010). In this study, the mean OC/EC ratio was 3.58, much higher than that of Thessaloniki port in Greece and Hong Kong, which indicates a worse influence of ship emissions in JT.

10. Figure 8. There should be an explanation to what is meant by the different "classes" in the Figure caption.

Response:

Thanks for your suggestion. The categorization of "classes" are described in page 10 line 15 as "Samples were categorized into three batches based on the $PM_{2.5}$ limit of AQI level (HJ 633-2012) during sampling, considering the influences of ambient pollution on particulate chemical composition". And for convenience of readers, we add the explanation in the title of Figure 8.

Revision in manuscript:

Figure 8: Enrichment factor of elements in $PM_{2.5}$ in JingTang Harbor. The classes are corresponding AQI level computed from $PM_{2.5}$ concentration during sampling time. The mean, minimum, and maximum concentrations of each element are also illustrated.

Reference

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