Dear Editor and Reviewers:

Thank you very much for your comments on our manuscript [acp-2018-255]. We acknowledge the suggestions of two anonymous reviewers and are grateful to your efficient serving. We have updated the manuscript based on these valuable comments and suggestions, and the point-by-point responses are listed below.

Referee #1

General comments:

The authors focused on air quality along the Yangtze River based on a shipboard observation performed in winter of 2015. Over the past few decades, China's rapid development leads to huge cargo transports in the Yangtze River channel. However, there is lack of data for ship emission along the Yangtze River channel, especially in the inland area. From this viewpoint, this manuscript supplied value data and made some contributions to portray a picture of air pollution along the Yangtze River. However, the manuscript suffered from poor English written. There are a lot of wrong spelling, tedious sentence, vague expression. Generally, the manuscript is difficult to read and should be improved greatly before publication.

Response: Thank for reviewer's valuable comments. In the new version, we have updated the manuscript on the basis of the comments. Especially, we have improved the English presentation greatly, including grammar and typing mistake throughout the manuscript.

Specific comments:

1), Line 4 what mean "onboard and coastal areas".

Response: It means "people living along the Yangtze". This sentence has been changed to "Air quality over the Yangtze River is interesting as it may have significant influences on the aquatic ecosystem, the health of everyone living along the Yangtze River, and regional climate change."

2), Line 7 After the sentence of "Based on the filter samples,", the PM2.5 concentration

during the cruise campaign should be shown.

Response: We have added the PM_{2.5} in Abstract. "The total average concentration of PM_{2.5} were 119.29 \pm 33.67 µg m⁻³, and the dominate ionic composition in PM_{2.5} was were SO₄²⁻ with the average

concentration of $15.21 \pm 6.69 \ \mu g \ m^{-3}$, followed by one of NO_3^{-1} ($13.76 \pm 4.99 \ \mu g \ m^{-3}$), NH_4^+ ($9.38 \pm 4.35 \ \mu g \ m^{-3}$), $Ca^{2+}(2.23 \pm 1.24 \ \mu g \ m^{-3})$ in this cruise."

3), Line 44-55 Authors cited a few of literatures focused on air quality on the region of Yangtze River Delta. In my opinion, authors should expand these literatures to the MLYR region, of which is overlapped well with the present region. Furthermore, the author should show specific regions shown in cited literatures.

Response: This was changed. To best our knowledge, numerous studies have been conducted in megacities in the MLYP region, especially Nanjing and Shanghai. Of course, there are also many papers which were related to air quality in other cities or rural in YRD region. However, we still thought long-time observation and sampling on air quality were only focused in Nanjing and Shanghai.

4), Line How about the T/B values for EP3 and EP5?

Response: We have re-calculated our data, and new results have been changed in the new manuscript in Table 2. Air mass with T/B ratio ≥ 2 were identified from fresh emissions. As shown in Figure S2, the peak value of T/B ratio clearly performed in EP-3 and EP-5, suggesting fresh emission dominant.



Figure S2. Time series of meteorological parameters during YRC (T and RH). (b) Time series of ratio of Toluene to Benzene.

5), Line 214 there are two "with". This sentence should be written.

Response: This sentence has been changed to "The local air during EP-4 was in low pressure system with low wind speeds that didn't favor the diffusion of the local pollution".

6), Line 292-293 "....., accounting for 37.43% and 40.15% in PM_{2.5} and PM_{1.0}?", gained in the present study?

Response: Yes, these data all acquired from this cruse. This sentence has been changed to "....., accounting for 37.43% and 40.15% in PM_{2.5} and PM_{1.0} during YRC, respectively"

5, Line 462 ".....and the YDR, Jiangsu, east of Anhui, and the Mongolian plateau were identified as the major source regions, and pathways." This sentence should be rewritten.

Response: this sentence has changed to "Fine particles Ni (Figure 6i) had almost same spatial distribution with Cr, that Shanghai, Jiangsu, and East of Anhui, and the Mongolian plateau were identified as the major potential source regions or pathways, owing to ship emissions, nonferrous metal mining, and smelting industries. The Mongolian plateau also was a source region, indicating that nature dust may be possible source for Cr and Ni."

Technique corrections:

- (1) Line 3 "River" is changed to be "river".
- (2) Line 11 "the secondary inorganic formation" should be changed to "the secondary inorganic aerosol formation".
- (3) Line 19 "This result....." should be changed to "The results".
- (4) Line 35 "their effects" should be changed to "their negative effects".
- (5) Line 40 "……and possible sources in this region have been generally characterized" should be changed to "……and source identification in this region have been generally studied".
- (6) Line 63 "The MLYR" should be changed to "The MLYR region", and "effecting its air quality" should be deleted.
- (7) Line 68 "particle matter" should be abbreviated to be "PM".
- (8) Line 77 "noted" should be changed to "pointed out".
- (9) Line 79 "Shanghai port" should be changed to "The Shanghai port".
- (10) Line 83 "the air quality" should be changed to "air quality".
- (11) Line 93 "to the best of our knowledge, it is the first systematic observation to characterize the air pollution along the China's largest and longest river" should be changed to "to the best of our knowledge, it is the first systematic observation on air pollution along the Yangtze River".
- (12) Line 97 "A mobile haze monitoring platform" should be changed to "A mobile monitoring platform".
- (13) Line 204-205 A sentence should be added here to explain the T/B value for weather

identification, although it has been explained in the Experimental section.

- (14) Line 206 "supplements" should be changed to "supporting information".
- (15) Line 217 "in the sixth episode" should be changed to "For the sixth episode".
- (16) Line 233 "Their detail information" should be changed to "The detailed information".
- (17) Line 245 "....., mainly owing to local emissions, photochemical processes and meteorology conditions (Xu et al., 2011)" should be deleted.
- (18) Line 247 "cities" was changed to "the cities".
- (19) Line 252 "was substantially enhanced" should be changed to "increased".
- (20) Line 261 "the mean levels" should be changed to "the mean level".
- (21) Line263 "revealed" should be changed to "was characterized by".
- (22) Line 264 "edge" should be changed to "banks".
- (23) Line 266 "by" should be changed to "identified by".
- (24) Line 268 "regionally" should be changed to "apparently".
- (25) Line 430 "the similar source region distributions" should be changed to "the similar region distributions".
- (26) Line 542 "It is noted that" should be changed to "It was noted that".
- (27) Line 564 "the YRD regions" should be changed to "the YRD region".
- (28) Line 567 "Ship engine emission" should be changed to "Ship emission".

Response: We have followed these valuable suggestions and made the corrections accordingly.

Referee #2

General comments:

General comment: This manuscript aims to provide a good picture of air pollution in the Mid-Lower Reaches Yangtze River (MLYR) based on a 15-day cruise campaign in winter of 2015. With chemical speciation data from filter samples, sources impacting the MLYR region are discussed including coal combustion, ship emission, biomass burning etc. Although these are important data, there are still some limitations of this work. One is the number of samples is limited, and the other is that in the data analysis section, it is pretty descriptive. Instead, there should be more in-depth discussion and it should be more logic and structured. With the current information provided in the manuscript, it is hard to draw firm conclusions. Therefore, I suggest the authors to revise the manuscript with in-depth data analysis and provide clear and new conclusions.

Response: We thank the reviewer for their helpful comments and suggestions, which are helpful for the improvement of the manuscript. We also have in-depth re-analyzed our data and revised the manuscript carefully according to the reviewer's comments.

Specific comments:

1). Why is levoglucosan from satellite data instead of from filter samples? What about the spatial resolution of satellite data? The authors indicate that biomass burning may make a big contribution to rural area. It will be more interesting to know the quantitative contribution from biomass burning.

Response: Thank for reviewer's valuable comments. The mass concentration of levoglucosan were analyzed from filter samples (PM_{2.5}) by IC methods. We just acquired the value aerosol optical depth (AOD), and SO₂, CO, NO₂ column concentration from Satellite data. We have added spatial resolution of satellite datasets in section 2.4. "Based on spatial interpolation methods, all of data from satellite datasets were interpolated and averaged into grid cells with a $0.25^{\circ} \times 0.25^{\circ}$ resolution".

Thank you for interesting in biomass burning event in rural region along over MLYP region. As you suggested, we also try to quantify the contribution of biomass burning to particulate matter. In general, both K⁺ and levoglucosan (lev) could be regarded as tracers for biomass burning. However, significantly correlation between Ca^{2+} and K⁺ suggested that dust could be the major source of K⁺ in PM_{2.5} sampled during YRC. Meanwhile, numerous studies have confirmed that lev mostly originate from biomass burning. Hence, the levoglucosan concentration and ratio of OC to lev (OC/lev) were widely used to estimate the contribution of biomass burning to organic carbon. The detailed information will be added in section 3.4.4 "The levoglucosan concentration and ratio of OC to lev (OC/lev) were widely applied to estimate the contribution of biomass burning to organic carbon in PM_{2.5}. To further quantify the contribution of biomass burning to OC, an empirical model was utilized as proposed by Wan et al. (2017):

$$OC_{BB} = \left(\frac{[lev]}{[OC]}\right)_{ambient} / \left(\frac{[lev]}{[OC]}\right)_{BB} (5)$$

The differences of the (lev/OC) $_{BB}$ ratio among different biomass fuels and combustion conditions were taken into account. So, the average (lev/OC) $_{BB}$ ratio of 8.14 % was selected to calculate the contribution

of BB to OC (Wan et al., 2017). Figure S9 presents the variation of lev/OC ratio along the Yangtze River. The ratio of lev/OC during this cruise ranged from 0.03 % to 0.91 % with an average of 0.35 \pm 0.24 %, which was comparable to that of Lin'an in YRD region (Liang et al., 2017). However, the ratio of lev/OC during YRC was near an order of magnitude of lower than its value in New Delhi (3.1 \pm 0.8 %) (Li et al., 2014) and Lumbini (3.34 \pm 2.53 %) in the northern edge of Indo-Gangetic Plain (Wan et al., 2017), where BB play an important role on air quality. Figure S9 also shows the time serious of contribution of BB-OC to OC. The average contribution of BB-OC/OC was 4.26 \pm 2.89 %, while the mean mass fraction of OC to PM_{2.5} was slightly higher than 20%. The peak contribution of OC deriving from BB to total OC of PM_{2.5} nearly accounted for 11% in EP-6, which was approached that of the Pearl River region sites (13%) (Ho et al., 2014). Here, it's emphasized that our method based on empirical formula and value is just rough estimation. Hence, the radiocarbon measurement (¹⁴C) of carbonaceous aerosol and air quality model simulation should need to confirm this result in the future.



Figure S9. Time serious of Lev/OC and Lev/ $PM_{2.5}$ ratios, and contribution of BB-OC to OC and $PM_{2.5}$ during YRC.

2). The influence of ship emission on PM_{2.5} in urban city is an important question. The authors claim that the ship plume could contribute to more than 50% of the total PM_{2.5} in the Shanghai ports. As there are quite a few assumptions, how to validate such result (50% of the total PM_{2.5})?

Response: Thank for reviewer's valuable comments. As your stated above, the ship emissions have become an important pollution sources in the port cities. The Yangtze River Campaign give us a valuable opportunity to study ship emissions along the biggest and busiest river in China. In present study, we try to evaluate and quantify ship emissions along Yangtze River. Firstly, the emission factors of heavy metal from four different oil were analyzed in our lab. V are only detected in heavy oil. Although both Ni and V were frequently regarded as tracers for heavy oil, only V was selected as a tracer for heavy fuel oil in

present study. Next, the primary ship emissions were re-analyzed and calculated. It was presented in section 3.5.1. However, numerous studies also pointed out that this method underestimate the contribution of ship emissions, due to lack of rare elements such as:Tb, Er, Yb, and Lu. Besides, ship plume also released larger amount of NO_X, SO₂, and VOCs, which all are precursors for secondary aerosol. Hence, we try to access the contribution of ship emissions to secondary aerosol. The limit ratio of SO₄²/V, NO₃/V, and OC/V were used to evaluate the SO₄², NO₃, and OM from ship emissions. We thought it is still reliable method to estimate the concentration of sulfate and OM deriving from HFO ship emissions. However, chemical process of NO_X to nitrate is complex and contribution nitrate originating from ship emissions were high variable. Recently, many studies have verified that nitrate has become dominant components in PM_{2.5} collected in Shanghai. Hence, other mobile sources (except ship emissions) also may be important sources for nitrate in PM_{2.5}. "However, it is worth noting that our estimation based on empirical values were limited by meteorological conditions and sample numbers. Hence, long-term observation and high resolutions model simulation of ship emissions should be strengthened along the Yangtze River, especially in Shanghai harbor clusters."

3). There are many typos in the manuscript and it requires careful revision. It is clear that there is a need to improve English in the manuscript.

Response: Thank your valuable suggestion. In the new version, we have improved the English presentation greatly, including grammar and typing mistake throughout the manuscript.

Reference:

Ho, K. F., Engling, G., Sai Hang Ho, S., Huang, R., Lai, S., Cao, J., and Lee, S. C.: Seasonal variations of anhydrosugars in PM_{2.5} in the Pearl River Delta Region, China, Tellus B: Chemical and Physical Meteorology, 66, 22577, 10.3402/tellusb.v66.22577, 2014.

Li, J., Wang, G., Aggarwal, S. G., Huang, Y., Ren, Y., Zhou, B., Singh, K., Gupta, P. K., Cao, J., and Zhang, R.: Comparison of abundances, compositions and sources of elements, inorganic ions and organic compounds in atmospheric aerosols from Xi'an and New Delhi, two megacities in China and India, Sci. Total Environ., 476-477, 485-495, 10.1016/j.scitotenv.2014.01.011, 2014.

Liang, L., Engling, G., Zhang, X., Sun, J., Zhang, Y., Xu, W., Liu, C., Zhang, G., Liu, X., and Ma, Q.: Chemical characteristics of PM_{2.5} during summer at a background site of the Yangtze River Delta in China, Atmos. Res., 198, 163-172, 2017. Wan, X., Kang, S., Li, Q., Rupakheti, D., Zhang, Q., Guo, J., Chen, P., Tripathee, L., Rupakheti, M., Panday, A. K., Wang, W., Kawamura, K., Gao, S., Wu, G., and Cong, Z.: Organic molecular tracers in the atmospheric aerosols from Lumbini, Nepal, in the northern Indo-Gangetic Plain: influence of biomass burning, Atmos. Chem. Phys., 17, 8867-8885, 10.5194/acp-17-8867-2017, 2017.

Air quality in the middle and lower reaches of the Yangtze River channel: A cruise campaign

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1 Abstract

2 Yangtze River is the longest river in China, nearly one-third of the national population lives along the 3 river. Air quality over the Yangtze River is interesting as it may have significant influences on the aquatic 4 ecosystem, health of everyone living along the Yangtze River, and regional climate change. Chemical 5 compositions of ambient aerosol were determined during a comprehensive cruise campaign carried out 6 along the Mid-Lower Reaches Yangtze River (MLYR) in winter of 2015. The total average concentration of PM_{2.5} were 119.29 \pm 33.67 µg m⁻³, and the dominate ionic composition in PM_{2.5} was were SO₄² with 7 an average concentration of 15.21 \pm 6.69 μg m^3, followed by NO_3^{\circ} (13.76 \pm 4.99 μg m^3), NH_4^{\circ} (9.38 \pm 8 9 4.35µg m⁻³), Ca²⁺(2.23 \pm 1.24µg m⁻³) in this cruise. Based on the filter samples, the concentration and 10 chemical composition of PM_{2.5} were remarkably varied or fluctuated from coastal areas to inland over 11 the MLYR region. Crustal elements (Ca, Mg, Al and K) from floating dust showed peak concentrations 12 in the Yangtze River Delta (YRD) region, while secondary inorganic species (SO_4^{2-} , NO_3^{-} and NH_4^{+}) and 13 some most enriched elements (Pb, As, Se and Cd) presented the high levels in central China (Wuhan 14 region). The significantly correlation between Se and SO₄²⁻ suggested that coal combustion may play an 15 important role in secondary inorganic aerosol formation. The relative high enrichment factors (EFs) of 16 Ca (EFs > 100) suggested the crustal elements may derive from anthropogenic sources. Furthermore, the 17 concentration of levoglucosan in PM_{2.5} and CO column level from satellite observation greatly enhanced 18 in the rural areas (Anhui and Jiangxi), indicating that biomass burning may make remarkable contribution 19 to the rural area. The concentrations of typical tracer for heavy oil (V and Ni) significantly increased in 20 the Shanghai port, that was mainly ascribed to the ship emission, based on the air mass source analysis 21 and the relatively high ratio of V/Ni as well. The results shown herein portrayed a good picture of air 22 pollution along the Yangtze River.

23 Keywords:

24 Shipboard observation, chemical composition, ship emission, Mid-Lower Yangtze Plain

25 1 Introduction

Yangtze River is the longest river in China, originating from the Qinghai-Tibetan Plateau and extending
to the East China Sea, and it drains an area of 18,08,500 square km basin, of which is China's great
granary, and feeds nearly one-third of the national population (Liu et al., 2007; Jiang et al., 2008).
Currently, three densely city agglomerations, including Wuhan, Nanjing, and Shanghai (WNS), which

are the centers of economy, transportation, politics, and culture in central and eastern China, and all of which are home to larger petrochemical complex and/or steel industry, have formed along both shores of the Mid-Lower Reaches Yangtze River (MLYR). The MLYR region is one of the most developed and economically vibrant regions in China, accounting for 34.13% of China's total GDP in 2015. Owing to fast economic development and industrialization, this region has become one of the most polluted areas in China (Xu et al., 2016b).

36 Fine aerosol particles are becoming more important in recent years, due to their negative effects on 37 human health, agriculture, and climate change (Wang et al., 2012; Kang et al., 2013b; Pöschl, 2005; 38 Seaton et al., 1995; Ackerman et al., 2004; Stier et al., 2005; Chameides et al., 1999; Novakov and Penner, 39 1993; Jones et al., 1994). Numerous field observations related to fine particles have been conducted in 40 the megacities in the Yangtze River Delta (YRD) region, especially in Nanjing and Shanghai. Over the 41 past years, the variation of mass concentrations, chemical compositions, size distributions, seasonal 42 variations, daily change, optical properties, and temporal-spatial distributions of fine particles in this 43 region have been investigated, and the causes and impacts of aerosol pollution have also been generally 44 studied (Zhou et al., 2016; Kang et al., 2013b; Tao et al., 2014b; Shen et al., 2014; Fu et al., 2014; Huang 45 et al., 2013; Huang et al., 2012b; Huang et al., 2012a; Ding et al., 2013a; Ding et al., 2017; Zhang et al., 46 2010). By analysis of several serious haze cases, Huang et al. (2012) pointed out that secondary inorganic 47 and dust episodes always erupted in spring, while biomass burning (BB) event was often observed in 48 summer (harvest season for wheat). Further, the high sulfate oxidizing rate (SOR) and nitrate oxidizing 49 rate (NOR) were also observed from long-term field measurements in Nanjing and Shanghai, indicating 50 that photochemical reactions in the atmosphere were quite active in these areas (Zhou et al., 2016; Zhou 51 et al., 2017; An et al., 2015). Wang et al. (2015b) also found that secondary pollutants contributed the 52 major fraction of aerosol mass, especially in Shanghai-Nanjing city cluster. The increasing trend of the 53 NO_3/SO_4^2 rations since 2000 suggested that vehicle sources became more important in this region (Kang 54 et al., 2013a; Huang et al., 2012a; Tao et al., 2014b; Sun et al., 2017). Beyond, Cheng et al. (2014) 55 estimated that BB contributed 37% of PM2.5, 70% of organic carbon, and 61% of element carbon in 56 harvest, respectively. If BB was controlled and even forbidden in this season, the PM_{2.5} levels would 57 decrease by 47% in the YRD region (Cheng et al., 2014). Some typical events, including fresh 58 combustion pollution from firework (Zhang et al., 2010; Kong et al., 2015), and the peak of secondary 59 inorganic aerosol species (SNA, SO_4^2 , NO_3 , and NH_4^+) deriving from the travel rush and re-opening of

factories after China Spring Festival (Huang et al., 2012b; Kong et al., 2015), have also been focused and analyzed. Huang et al. (2013) also investigated the chemical composition of fine particles in Shanghai, finding that the concentrations of anthropogenic calcium drastically decreased as results of strict monitoring and implementing control of construction activity during 2010 Word Expo. Compared with normal (pre-control) periods, the levels of Ca^{2+} and SO_2 also reduced 55% and 46% during the 2014 Youth Olympic Games, respectively (Zhou et al., 2017).

66 The MLYR region faces the most complex anthropogenic emission sources, including a variety of 67 power plants, large petrochemical and steel industries, and farmland distributed along both banks of the 68 Yangtze River, as well as ship emissions. It was well documented that ship emissions displayed a 69 significant impact on regional air quality, particularly in traffic hubs and harbors (Pandis et al., 1999; 70 Becagli et al., 2017; Zhan et al., 2014). The contribution and effect of ship emissions to local air pollution, 71 especially PM, have been briefly analyzed at levels from regional to global (Jalkanen et al., 2015; Zhan 72 et al., 2014; Pandis et al., 1999; Fan et al., 2016; Coggon et al., 2012). The emission factors, and 73 properties of emitted particles and gases from ship-plume in different engine speeds were also reported 74 (Zhang et al., 2016; Moldanová et al., 2009; Agrawal et al., 2009). Ship-related pollutants have been identified in the YRD port cluster and surrounding area. In 2010, SO₂, NO_x, and PM_{2.5} from ship 75 emissions in the YRD port cluster were up to 3.8×10^5 t/y, 7.1×10^5 t/y, and $5.1 \times$ t/y, respectively. The 76 77 maximum SO₂ and NOx concentrations from the ship in harbors or traffic hubs were nearly 36 times and 78 17 times higher than the maximum land-based emissions, respectively (Fan et al., 2016). Zhao et al. 79 (2013b) pointed out that Ni and V enriched in submicron particles in Shanghai port. Recently, Liu et al. (2017) also reported that ship-plume contributed to 2-7 µg m⁻³ to fine particle within the coastal of 80 81 Shanghai port, accounting for 20-30% of total PM_{2.5}. Known as "golden canal", Yangtze River was an 82 important route for trade and travel. However, there is seldom data related to air quality and the influence 83 of ship emissions along the Yangtze River channel. Meanwhile, related observations with the 84 synchronous trend of aerosol in the MLYR region remain insufficient.

To characterize air quality in this region, a round-trip field observation voyage, namely Yangtze River Campaign (YRC), was carried out between Shanghai and Wuhan. This cruise aimed to characterize the chemical components of atmospheric pollutants, to analyze these spatial distributions, and to identify potential source contribution. To the best of our knowledge, it is the first systematic observation on air pollution along the largest and longest river in China.

90 2 Measurements and methods

91 **2.1 Overview YRC**

92 A mobile monitoring platform (A container: length 10.0 m, width 4.0 m, and height 2.5m) was placed on 93 a vessel (length: 20 m, width 6 m), sailing from 22 November to 05 December in 2015 along the Yangtze 94 River channel between Shanghai to Wuhan (29.72°N-32.33°N, 114.33°E-121.61°E). This campaign route 95 is illustrated in Figure 1. Starting on 22 November in the Waigaoqiao port of Shanghai, then the vessel 96 crossed Jiangsu, Anhui province, and finally arrived at the Hankou port in Wuhan, Hubei province on 29 97 November along the Yangtze River waterway. The ship shifted at an average speed of 1 m/s heading the 98 upper the Yangtze River towards Wuhan. After berthing in the port of Wuhan one night, the vessel turned 99 around, departed, and shifted towards Shanghai. This cruise finally ended in the Waigaoqiao port in 100 Shanghai on 5 December. During YRC, a wide range of data, including common meteorological 101 parameters, trace gas concentrations (CO, NO-NO_x, SO₂, and O_3), chemical composition of aerosol 102 particles, and satellite dataset over this region were acquired and analyzed.

103 2.2 Trace gases measurements

A serious of commercial trace gas instruments, including 43i SO₂ analyzer, 49i O₃ analyzer, 48i CO analyzer, and 42i NO-NO₂-NO_x analyzer (Thermo Environmental Instruments Ins., USA C-series), were installed in an air-conditioned container to measure the concentration of gaseous pollutants. The routine procedures of QA/QC (the daily zero/standard calibration) were performed, according to the technical guidance by U.S. Environmental Protection Agency (USEPA, 1998).

109 Trace alkanes, including toluene and benzene, were also sampled in stainless summa canister, and 110 quantified by a gas chromatograph with a mass spectrometer and a flame ionization detector (GC-111 MS/FID) (Wang et al., 2014). The sampling interval of VOCs was 3 hours with fluctuation. The ratio of 112 toluene/benzene (T/B) was commonly regarded as an indicator of the photochemical processing 113 (Baltrenas et al., 2011). The high ratio of T/B indicated that air masses were fresh emissions, while lower 114 value suggested that air masses had undergone photochemical processes. In this paper, we used the same 115 value ratio of T/B in CalNex (Gaston et al., 2013). Air masses with T/B << 1 were excepted to well 116 undergo photochemical aging while urban fresh air masses had much higher T/B ratio (≥ 2). Ship track 117 self-emission was removed by subducting the periods when the winds blew from the stern, that is, the

118 relative wind direction was from 130° to 220° to the ship direction (0° in the front). The real-time

119 measurement of trace gases and aerosol data presented here were filtered out by this method.

120 **2.3 Chemical analysis of the filter samples**

121 Particulate samples of $PM_{2.5}$ and $PM_{1.0}$ were simultaneously collected on separate quartz filters (Φ 90 mm, 122 Whatman Inc., Maidstone, UK) using a medium-volume sampler by HY-100 (Oingdao Hengyuan S.T. 123 Development Co., Ltd, China) (model: PM_{2.5}/PM_{1.0}; flow rate: 100 L min⁻¹, respectively), which was 124 placed on the foredeck at approximately 3.0 m above sea level. The duration time of collecting sample 125 was generally set at 12 h (in parallels: day 07:00-19:00, night 19:00-07:00), while it was also collected PM for 24 h. High-purity quartz filters were preheated at 500 °C for 10 h to virtually eliminate the 126 127 residues prior to sampling. All the samples were stored in a refrigerator keeping at -20 $^{\circ}$ C for analysis. 128 The filter sample masses were measured by an intelligent weight system (Hangzhou Wmade Intelligent 129 Technology co., LTD) which was maintained in constant condition (T: 20 °C and RH: 40%). All the 130 procedures were well documented, and supervised to avoid the possible contaminations. The sample 131 instruments were placed on the bow of the ship far away from its track. Ship self-emission in the filter 132 samples was ignored, since the most prevailing winds blew from the bow to the stern during the sampling 133 periods.

134 One-eighth of each filter was extracted ultrasonically by 20 mL of deionized water (18.2 M Ω cm⁻¹) for 40 min. After filtering, eight inorganic ions (SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, Na⁺, K⁺, Ca²⁺, and Mg²⁺) were 135 136 analyzed by an ion chromatography (940 Professional IC, Metrohm, Switzerland), and a sugar column 137 coupled with pulsed electrochemical detection (945 Professional Detector Vario, Metrohm, Switzerland) 138 was used to measure levoglucosan (lev) in the extract. Both of instruments were controlled with a 139 Professional IC software. The lower and upper limits of the detection were 0.5 and 4 μ g m⁻³, respectively. 140 The relative standard deviation of each ion was less than or equal to 2% from three reproducibility tests. 141 Blank samples were analyzed with the same processes to remove potentially contaminations.

One-eighth of the sample filter and the blank filter were cut into fragments, and digested at 170 °C for 4 h in a high-pressure Teflon digestion vessel with 3 mL of HNO₃ and 1 mL of HClO₄ (Wang et al., 2006; Li et al., 2015b). After cooling, the digested solution was filtered and diluted to 15 mL with ultrapure Mill-Q water. An inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7500a) was employed to measure the concentrations of 17 elements (Al, As, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Se, Tl, Pb, V, and Zn) in the filter samples. National standard material (soil, GSS-12, China) was also digested, and used to calculate the element recoveries ranging from 91%-102%. The detection limits of the trace elements were derived from the standard deviation (3 δ) of the blank values. Details relating to

150 ICP-MS have been described in elsewhere (Li et al., 2015b).

Organic carbon (OC) and elemental carbon (EC) in the aerosol samples were analyzed by a Thermal/Optical Carbon Analyzer (DRI Model 2001). Each sample was identified as four OC fractions (OC1, OC2, OC3, and OC4 at 120, 250, 450, and 550 °C, respectively, in a helium-air) and three EC fractions (EC1, EC2, and EC3 at 550,700, and 800 °C, respectively, in the mixture air (98% helium and 2% oxygen) by an IMPROVE thermal/optical reflectance (TOR) protocol. Pyrolyzed organic carbon (POC) was separately detected by transmittance. IMPROVE OC was defined as OC1 + OC2 + OC3 + OC4 + POC, and EC was calculated by EC1 + EC2 + EC3 – POC.

158 2.4 Satellite data and ship traffic data

159 The satellite databases, including Moderate Resolution Imaging Spectroradiometer (MODIS) with a 160 resolution of 10×10 km, Measurement of Pollutants in the Troposphere (MOPITT) and Ozone 161 Monitoring Instrument (OMI) on the National Aeronautics reaching a spatial resolution of 13×24 km at 162 nadir, and Space Administration's Earth Observing System (NASA's EOS) Aura satellite, were applied 163 to provide spatial distribution of aerosol particles and trace gases (Xu et al., 2011; Huang et al., 2012a). 164 The column levels of CO, NO₂, SO₂, and aerosol optical depth (AOD) were retrieved over the MLYR 165 region. In this study, all of data from satellite datasets were interpolated and averaged into grid cells with 166 a $0.25^{\circ} \times 0.25^{\circ}$ resolution.

Ship positions and numbers in the Yangtze River channel were decoded by Automatic Identification
System (AIS) databases which were obtained from the Marine Department. A 15-day AIS datasets along
the Yangtze River were selected with a high time resolution (about 15min).

170 **2.5 Potential source contribution function**

The potential source contribution function developed by Hopke et al. (1995) was applied to derive the potential source regions and spatial distributions. In this study, 3 day back trajectories arriving at height of 500 m was calculated using National Oceanic and Atmospheric Administration's (NOAA's) Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT-4) model (http://www.arl.noaa.gov/ready/ open/hysplit4.html) with global meteorological data from NCEP reanalysis data (ftp://arlftp.arlhq.noaa. 176 gov/pub/archives/rean-alysis) (Draxler and Hess, 1998). The contribution of the potential sources during

177 YRC was calculated by the PSCF analysis with TrajStat (Wang et al., 2009). The domain sources were

178 restricted to 25°N-45°N and 110°E-125°E, which were divided into grid cells with a 0.5°×0.5° resolution.

179 The PSCF value for the *ij* th grid cell was defined as:

180
$$\operatorname{PSCF}_{ij} = \frac{M_{ij}}{N_{ij}} W_{ij}(1)$$

where N_{ij} is the total number of trajectory segment endpoints that fall in the *ij* cell, and M_{ij} is the number of endpoints for the same cell with arrival times at the sampling site, corresponding to pollutant concentrations higher than an arbitrary criterion value. In this study, the average concentration for each trace element was set as the criteria value. To reduce the random error and uncertainty of the small value of n_{ij} , the weighting function of W_{ij} reduced the PSCF values when the total number of the endpoints in a particular cell n_{ij} was less by approximately 3 times than the average N_{Ave} value of the endpoints per each cell (Han et al., 2005):

188
$$W_{ij} = \begin{cases} 1.00 & N_{ij} > 3N_{Ave} \\ 0.70 & 1.5N_{Ave} < N_{ij} \le 3N_{Ave} \\ 0.42 & N_{Ave} < N_{ij} \le 1.5N_{Ave} \\ 0.17 & 0 < N_{ij} \le N_{Ave} \end{cases} (2)$$

189 **3 Results and discussion**

190 **3.1 Classification of the typical pollution episodes**

191 The air pollution during the cruise was classified into eight distinct episodes, based on sampling locations, 192 backward trajectories, and photochemical processes (T/B value) (Figure 1, Figure S1, Figure S2 and 193 Table 1). The detailed meteorological information over the MLYR region was also summarized in the 194 supporting information. As shown in Figure S1, the first episode (EP-1), starting from 22 to 23 November, 195 was characterized by the sampled air masses which came from the East China Sea, and were typically 196 influenced by the local industry and Shanghai harbor pollution. The ratio of T/B ranged from 0.6 to 2 197 with an average of 1.3, suggesting fresh air masses mixed by the aged ones. The air masses in the 198 secondary episode (EP-2), with B/T<1, originated from the rural areas (Anhui and Henan), carrying 199 agriculture emission (Figure S2). Sampled air masses stagnated around Jiujiang to Wuhan from the third 200 episode (EP-3) to the fifth episode (EP-5). However, the fourth episode (EP-4) (Wuhan region) with the 201 low average T/B ratio of 0.97 undergone well atmospheric aging. The local air during EP-4 was in low

202 pressure system with low wind speeds that didn't favor the diffusion of the local pollution (Figure S3). 203 Air mass with T/B ratio ≥ 2 were identified from fresh emissions. Both EP-3 and EP-5 (nearly Jujiang) 204 were characterized by high T/B value (Figure S2), suggesting that these two pollution episodes were 205 contributed mainly from regional fresh emissions. For the sixth episode (EP-6), the wind direction shifted 206 from southwest to northwest, and the vessel was again traveling through the rural area of middle reach 207 of Yangtze River, suggesting that air masses may originate from agricultural activities. Then in the 208 seventh episode (EP-7), a cold front arrived, and wind speeds increased significantly from average 3.84 209 m/s to 5.38 m/s (Table 2) with air masses transported from northern inland regions, which was further 210 confirmed by wind fields (Figure S3) and the sharply decreases of RH (Table 2). The last episode (EP-211 8) was in the YRD region where highly intensive anthropogenic activities released a large amount of the 212 pollutants. Air masses in EP-8, with the average T/B value of 1.73, were expected to mixture of aged 213 masses sources with regional fresh emissions. Overall, EP-1 and EP-8 (the YRD region) were mainly 214 influenced by fresh local emissions mixed with aged air masses, while agriculture emissions contributed 215 significantly to during EP-2 and EP-6 episodes. Both EP-3 and EP-5 were characterized by fresh 216 emissions, even though the megapolis was not available in this region. The cruise started on November 217 22, but the offline PM_{2.5} samples were collected after November 25. Thus, EP-1 description was ignored 218 in the present study.

219 **3.2 Air pollution during YRC**

220 **3.2.1 Variability of air pollutants observed in the vessel**

221 The PM_{2.5} and PM_{1.0} was sampled from 25 November to 5 December in 2015. The detail information is 222 also summarized in Table 1. The average mass concentrations of PM_{1.0} and PM_{2.5} during YRC were 96.69 223 \pm 22.18 µg m⁻³ and 119.29 \pm 33.67 µg m⁻³, respectively. The average ratio of PM_{1.0}/PM_{2.5} was 0.8 \pm 0.085, 224 implying that $PM_{2.5}$ mainly dominated by fine particles with the size of $< 1.0 \mu m$. The detailed 225 meteorological information, including temperature (T), RH, pressure, and wind speed (WS), and trace 226 gaseous in different episodes are also summarized in Table 2. The peak concentrations of PM_{2.5} were 227 observed in EP-4 and EP-7. However, there were obvious differences between EP-4 and EP-7 in the 228 meteorological parameters and trace gases levels, indicating that these two pollution events were 229 completely different. As mentioned in 3.1, sampled air masses in EP-4 mainly originated from local 230 emissions, whereas EP-7 was influenced by a long-transport of air pollution.

231 As shown in Table 2, the average concentrations of CO, SO_2 , and NO_X varied dramatically in the 232 different pollution episodes. Average concentrations of CO, and SO₂ (993.96 \pm 387.34, and 9.32 \pm 4.33 233 ppbv, respectively) were slightly lower than those in the cities in winter, including Wuhan (1024.00, and 234 13.30 ppbv) (Wang et al., 2017), Nanjing (1096.00, and 13.09 ppbv) (Sun et al., 2017), Chengdu (1440.00, 235 and 12.60 ppbv) (Liao et al., 2017), and Shanghai (1067.20, and 18.90 ppbv) (Huang et al., 2012a). CO 236 level continued to rise since the start of the YRC, and finally peaked in EP-6 and EP-7. Meanwhile the 237 SO_2 and NO_X levels were much lower in these two episodes, which were identified as the BB event. As previously reported, biomass burning could produce large amount of CO, while NO_X and SO₂ were not 238 239 the major gaseous pollutants released from BB (Huang et al., 2012a; Ding et al., 2013b). The mean CO 240 concentration in EP-7 reached to 1224.88 ppbv, which was close to the level recorded at Shanghai during 241 the harvest season of wheat (June) (Huang et al., 2012a). The SO₂ concentrations in EP-3 and EP-8 242 greatly increased, which were close to the SO_2 level in the haze event in Shanghai (Huang et al., 2012a). 243 This was partly caused by local fresh emissions (the high T/B in EP-3 and EP-8). Except EP-6 and EP-7 244 (BB event), the NO_X concentration almost exceeded 50 ppbv along this cruise. The NO_X concentration 245 peaked in EP-3, which was considered to mainly come from local emissions. The average mass 246 concentration of NO_x in this cruise is 63.74 ± 41.08 ppby, which was much higher than the mean level in 247 Shanghai (42.40ppbv, 2012) (Han et al., 2015), and Guangzhou (39.14ppbv, 2012) (Zou et al., 2015) that 248 represented typical urban NO_x level. The high NO_x level along YRC was determined to come from 249 strong regional emission. It could be derived that many sources of air pollution distributed on both banks 250 of the Yangtze River.

251 **3.2.2** Regional distribution of air pollutants identified by remote sensing observation

252 The MLYR region is one of the most polluted areas in China, and the spatial distribution of various 253 pollutants were apparently different from coastal to inland region. As shown in Figure 2a, the high 254 average values of AOD retrieved from MODIS MOD04 were observed in eastern Jiangsu and Shanghai, 255 etc, where human and industrial activities were concentrated, suggesting that anthropogenic emissions 256 were dominated. However, there was much missing data of AOD in central China due to heavy clouds. 257 As presented in Figure S4 of the MODIS true-color imagery on 28 November, thick clouds covered 258 across central China. Besides, the average of AOD was about 0.45, which was slight lower than that in 259 Shanghai in winter (0.55) (He et al., 2012), and background (0.65) in the North China plain (Xu et al., 260 2011). The AOD value in northern China was higher than that in southern China. As plotted in Figure

261 2b, CO surface mixing ratio calculated by MOPITT revealed that Shandong, Henan, and Anhui were 262 exposed to elevated CO column concentrations. CO is an important tracer for the incomplete combustion 263 sources, such as BB and fossil fuel combustions (Girach et al., 2014). BB should be major source for CO 264 in the grain-producing areas (Huang et al., 2012; Ding et al., 2013). As mentioned in section 3.2.1, the 265 peak CO level was also observed in Anhui and the west of Jiangsu (EP-6 and EP-7). However, the sources 266 of CO in the northern China should further study in the future. The high levels of SO₂ was mainly 267 observed in the east in Anhui and stretched to the Shanghai area (Figure 2c), suggesting high-sulfur fossil 268 fuel were still widely utilized over the MLYP region. Whereas, SO₂ levels in Nanjing urban areas were 269 measured at the background pollution levels. In general, NO₂ was regarded as a tracer for the local 270 emission source, due to short lifetime in the atmosphere (Geng et al., 2009; Xu et al., 2011). NOx 271 emissions significantly originated from vehicle and power plant (Fu et al., 2013). One can see that the 272 NO₂ emission was characterized by strong local sources in north China and the YRD region, which are 273 in good agreement with the previous reports (Lin, 2011; Zhao et al., 2013a).

274 **3.3** Chemical composition of fine particles during YRC and comparisons with other published data

275 The concentrations and mass fractions of the major ions and levoglucosan in PM_{2.5} are shown in Figure 276 3. The water-soluble ions constitute one of the dominant components in atmospheric aerosol and 277 determine the aerosol acidity (Kerminen et al., 2001), accounting for 37.43% and 40.15% in PM_{2.5} and 278 $PM_{1,0}$ during YRC, respectively. To access the data quality, ion balance gained by the major anions (SO $\frac{2^{2}}{4}$, NO₃, and Cl⁻) and cations (Na⁺, NH₄⁺, K⁺, Ca²⁺, and Mg²⁺) was calculated in this cruise. Both cations 279 280 and anions are in the units of equivalent concentration (μ eq m⁻³). There is a good correlation (R² > 0.99 281 and $R^2 > 0.98$, P < 0.01) between cation and anions (equivalent concentration) in PM_{1.0} and PM_{2.5}, respectively, implying a high quality of data and same source of major ions in this cruise (Figure S5a) 282 (Boreddy and Kawamura., 2015). Additionally, the relationship between NH_4^+ and $Ca^{2+} vs SO_4^{2-}$ and NO 283 284 was further investigated. As plotted in Figure S5b, the slopes of linear regression lines for $[NH_4^++Ca^{2+}]$ 285 vs $[SO_4^2 + NO_3^3]$ in PM_{2.5} and PM_{1.0} were 1.171 and 1.154, respectively, suggesting that the alkaline 286 substance in aerosol could completely neutralize SO_4^2 and NO_3^2 during YRC.

For the ionic concentration, the most abundant species of $PM_{2.5}$ was SO_4^{2-} with a mean of 15.21 ± 6.69 $\mu g \text{ m}^{-3}$, followed by NO_3^- (13.76 ± 4.99 $\mu g \text{ m}^{-3}$), NH_4^+ (9.38 ± 4.35 $\mu g \text{ m}^{-3}$), Ca^{2+} (2.23 ± 1.24 $\mu g \text{ m}^{-3}$), Cl^- (1.94 ± 0.92 $\mu g \text{ m}^{-3}$), Na^+ (1.29 ± 0.48 $\mu g \text{ m}^{-3}$), K^+ (0.63 ± 0.22 $\mu g \text{ m}^{-3}$), and Mg^{2+} (0.22 ± 0.07 μg

290	m ⁻³) (Figure S6a). The mass concentration of SNA accounted for 85.89% of the total water-soluble ions
291	in PM _{2.5} . Comparing with the previous reports (Figure 4), the SNA concentrations were much lower than
292	those collected in the western and northern polluted cities in winter, including Beijing (38.90, 22.70, and
293	22.4 μ g m ⁻³ , respectively) (Wang et al., 2015a), Xi'an (39.7, 21.43, and 12.50 μ g m ⁻³ , respectively) (Xu
294	et al., 2016a), Wuhan (29.80, 29.80, and 16.80 μ g m ⁻³ , respectively) (Zhang et al., 2015) and Chengdu
295	(31.80, 15.5, and 15.5 μ g m ⁻³ , respectively) (Tao et al., 2014a). However, the concentrations of SNA
296	were higher than those collected in marine boundary layer, such as East China sea (29.80, 29.80, and
297	16.80 μg m ⁻³ , respectively) (Nakamura et al., 2005), Northern South China Sea (7.80, 0.24, and 2.1 μg
298	m ⁻³ , respectively) (Zhang et al., 2007), South China sea (7.99, 0.08, and 1.083 µg m ⁻³ , respectively) (Hsu
299	et al., 2007), Taiwan Strait (5.20, 3.13, and 1.50 µg m ⁻³ , respectively) (Li et al., 2016), and Tuoji island
300	in Bohai Rim (8.90, 5.80, and 1.40 µg m ⁻³ , respectively) (Zhang et al., 2014). The SNA levels in the YRC
301	were close to Shanghai in winter (11.7, 13.33, and 8.11 µg m ⁻³ , respectively) (Zhou et al., 2016). The
302	mass ratio of NO_3^2/SO_4^{2-} was regarded as a marker to distinguish mobile source vs. stationary source
303	(Huang et al., 2013). The ratio of NO_3^2/SO_4^{2-} in this campaign was also close to that of Shanghai, and
304	lower than that in other cities (Figure 4), indicating that mobile source emissions (traffic) contributed the
305	most to fine particles. Besides, the mass concentration of SO_4^{2-} definitely exceed the level of $NO_3^{}$ in the
306	marine boundary layer (Figure 4), indicating that marine source was another important source for SO_4^{2-}
307	(Calhoun et al., 1991). The average concentration of $Ca^{2+}(2.23 \ \mu g \ m^{-3})$ in this cruise was the highest
308	among all locations and cruises (Figure 4), followed by Chengdu (2.10 μ g m ⁻³), Wuhan (1.90 μ g m ⁻³),
309	and Xi'an (1.33 μ g m ⁻³). As shown in Figure 4, Ca ²⁺ also presented the higher concentration in the cities,
310	and decreased from inland to coastal regions, indicating that Ca ²⁺ was mainly from terrace crustal (Xiao
311	et al., 2017). However, the concentrations of K^+ and Mg^{2+} for YRC were lower than those in the most
312	samples among all location (Figure 4). K ⁺ may originate from BB, sea salt, and crustal dust. The average
313	Cl ⁻ concentration during YRC was also lower than those in most cities (Figure 4). However, Na ⁺ level in
314	this cruise was higher than the most reported values (Figure 4). The poor correlation between Na^+ and
315	Cl ⁻ also indicated that two ions may have the different sources during YRC. Besides, the ratio of Cl ⁻ /Na ⁺
316	among all location (Figure 4) were much higher than 1.17 (ratio of seawater), suggesting that
317	anthropogenic sources, including BB and coal combustion, contributed the excessive Cl ⁻ in China cities
318	(Li et al., 2015a; Zhang et al., 2013). The concentration of levoglucosan, a BB tracer, ranged from 0.015-
319	0.18 μ g m ⁻³ with a mean value of 0.075 \pm 0.047 μ g m ⁻³ , much higher than the average concentration of

320 0.0394 μg m⁻³ in Lin'an (30.3°N, 119.73°E) (a rural site in the YRD region) (Liang et al., 2017),
321 indicating that BB was also a major contributor to PM_{2.5}.

322 17 elements of $PM_{1.0}$ and $PM_{2.5}$ were measured, and the average concentrations are summarized in 323 Table 3. For comparison, the data reported previously in the megacities (in winter) and the cruises are 324 also outlined in Table 4. Ca show the highest concentration among all elements (Table 3) at all locations 325 (Table 4), and shared 2.16% on average in PM2.5, partly due to cold front with floating dust in this 326 campaign. The secondary highest concentration among all elements was Fe (Table 3). This concentration 327 $(1.64 \ \mu g \ m^3)$ in the campaign was higher than those at many urban sites, such as Beijing $(1.55 \ \mu g \ m^{-3})$ (Zhao et al., 2013c), Shanghai (0.56 µg m⁻³) (Huang et al., 2012b), and Guangzhou (0.16 µg m⁻³) (Lai et 328 al., 2016), probably due to numerous steel industries/shipyards distributed on both banks of the Yangtze 329 330 River. Other elements decreased from K (865.88 ng m⁻³) to Tl (0.32 ng m⁻³). Pb and Zn contributed the 331 highest levels among heavy metals of PM_{2.5}. In addition to inland cities, such as Beijing (Zhao et al., 332 2013c), Wuhan (Zhang et al., 2015), and Chengdu (Tao et al., 2014a), the average concentrations of Pb 333 and Zn along the YRC were much higher than those in the other regions and cruises (Table 4). Both Pb 334 and Zn could originate from coal combustion and/or mineral industry, which were related to energy 335 structure and industrial layout over the MLYR region (Zhao et al., 2013c; Zhang et al., 2015; Tao et al., 336 2014a; Zhao et al., 2015).

337 The enrichment factors (EFs) were applied to distinguish crustal elements from the anthropogenic338 sources. The formula to evaluate EFs was:

 $EF_i = (X_i / X_R)_{aerosol} / (X'_i / X'_R)_{crust} (3)$

340 of which EF_i is the enrichment factor of element *i*; X_i and X_R are the concentrations of element *i* and 341 reference element of R in aerosol, respectively; X'i and X'_R are the background content of elements in 342 the MLYR soil (Wei et al., 1991). Al was considered to originate from soil. Hence, it was selected as 343 the reference element for the calculation. Trace elements of EFs < 10 included: Al, K, Mg, and Na, all 344 of which were regarded from crustal or re-suspension local soil. The species with higher EFs (10 < EFs)345 < 100) were thought to be the mixture of the crustal and anthropogenic sources, including Cr, Cu, Co, 346 Ni, and V. The elements of EFs > 100, including Ca, Zn, Se, Pb, As, Mo, Fe, and Cd, were attributed to 347 anthropogenic sources. To further explore sources of trace elements and potential geographical 348 distributions, PCA was used to classify the main source of trace elements of $PM_{2.5}$ using the rotate

349 component matrix and PSCF for individual element was performed to infer the potential source and/or 350 pathway regions. As shown in Figure 5a, trace elements were classified into four categories (PCA), which 351 could explain 86.73% of the variance, indicating that the major sources of elements of PM_{2.5} could be 352 considered and explained. More specifically, the first component (component 1) could account for 38.48% 353 of the variance, which was derived from coal combustion, including the high loadings of Cd, As, Pb, Tl, 354 and Se. Particularly, Se was generally considered as a tracer for coal combustion, due to its formation in 355 the high-temperature environment. Se produced by the rapid gas-to-particle conversion could undergo 356 long-range transport (Nriagu, 1989; Wen and Carignan, 2007). A significant correlation ($R^2 = 0.71$, P < 0.71357 (0.01) between SO₄²⁻ and Se is shown in Figure S6b. Furthermore, As and Pb mainly originated from coal 358 combustion after phasing out of leaded gasoline in China since 1997 (Xu et al., 2012), both of which had 359 significantly correlations with Se. The component 2 with a variation of 25.45%, contributed by the high 360 loading of Al, Mg, Ca, and K, all of which obviously represented the crustal or soil elements, and showed the low EFs values (EFs< 10, except Ca). Component 3, accounting for 15.14% of the variation, was 361 362 considered as the primary source of V, Co, and Ni. Both V and Ni were usually regarded as a tracer of 363 heavy oil combustion (Zhao et al., 2013b; Becagli et al., 2017). The fourth component (component 4) 364 showed the high loadings of Mn, Co, Zn, and Fe, all of which could explain 7.33% of the variance. Fe 365 exhibited the high EFs value, indicating that these may originate from anthropogenic sources. 366 Anthropogenic Fe was usually deemed to originate from steel factory and/or shipyard, both of which 367 were widely distributed along the Yangtze River (Fu et al., 2014). Their potential source contributions 368 and chemical processes would be detailed in section 3.4.

369 3.4 Regional difference in formation mechanism of aerosol pollution and potential source 370 contributions to element in PM_{2.5} over the MLYR region

371 3.4.1 Secondary component pollution related to coal combustion in central China

As illustrated in Figure 3, the mass concentrations of SNA with an average of $38.35 \pm 15.17 \ \mu g/m^3$ increased dramatically from coastal to inland cities and exhibited the highest level (#6, 79.06 $\mu g/m^3$) in Wuhan region (EP-4), accounting for nearly 50% of the local PM_{2.5} mass loading. As mentioned above, SO₂ and NO_x also presented the high concentration in this region. Furthermore, Wuhan and the surrounding regions were controlled by a low-pressure system with the low WS and high RH conditions (Figure S3), of which have been verified to cause haze episode (Zhao et al., 2013d; Quan et al., 2011; Wang et al., 2010). In addition, the ratio of $NO_3^2/SO_4^{2^2}$ in Wuhan area was close to the values of cities in northern China (relative low) (Figure 4), suggesting that the stationary sources (such as: coal-fired power station or stove emission) dominated in this region. Heavy clouds and high humidity in central China suggested aqueous phase transformation processes were probable the main reaction path of $SO_4^{2^2}$ from SO_2 (Wang et al., 2016; Zhao et al., 2013d). Besides, the mass fractions of SNA in PM_{2.5} also peaked in the rural region (EP-2 and EP-6), which was in accord with the low ratio of T/B in these regions, suggesting that aerosol particles in the rural region were well aged.

385 Meanwhile, trace elements for coal combustion (component 1) had also the high concentration in EP-386 4 and EP-5 (Figure 5b) when the ship anchored in Wuhan and traveled through the Jiujiang area. As 387 illustrated in Figure 6a-d, As, Cd, Pb, and Se showed the similar source distribution. The higher PSCF 388 values in Hubei, Hunan, and Jiangxi provinces coincided well with the uneven regional distribution of 389 the residential coal consumption (Figure S7) in central China, suggesting coal-related PM pollution was 390 quite serious in this region during this cruise. The peak mass fraction of Cl⁻ and SO₄²⁻ in PM_{2.5} in Wuhan 391 was also confirmed this result Thus, it's concluded that coal combustion contributed significantly to 392 serious pollution with the high SNA loading in Wuhan and the surrounding regions during sampling.

393 3.4.2 Mineral Dust in YRD region

394 Contrary to SNA distribution, the concentration of Ca^{2+} along this cruise increased from the mainland to 395 the costal of East China Sea (Figure 3). The peak concentration of crustal elements (component 2) and 396 Ca²⁺ mass fraction of PM_{2.5} occurred in EP-7 when a cold front arrived and associated with northeast 397 winds, accompanying with floating dust (Figure 3 and Figure 5b). In the Meantime, dust episode was 398 verified by the MODIS true-color image on 2 and 3 December (Figure S4), further confirmed by a drastic 399 decrease of RH with the prevailing northwest wind (Table 2 and Figure S3). As shown in Figure 6e-h, 400 the YRD region and the Loess Plateau with the highest PSCF values were identified as the important 401 source regions and/or pathways for crustal elements of Al, K, Mg and Ca. Meanwhile, central China also 402 showed the distribution of K and Mg, for which the coal combustion in this region could be primarily 403 responsible. Furthermore, Ca showed the high EFs (EFs > 100), suggesting that the crustal element may 404 not derive from natural source, but from anthropogenic re-suspension of road and/or construction 405 activities along the Yangtze River. To further evaluate the impact of anthropogenic Ca, the equation 406 below was applied:

$$Ca_{anthropogenic} = Ca_{total} - Al_{total} \times (Ca/Al)_{crust} (4)$$

407

408 (Ca/Al) _{crust} is the ratio of Ca to Al in the crust, and its value is 0.5. According to this method, the average 409 Ca _{anthropogenic} concentration was 2.15 μ g m⁻³, and the peak level reached to 3.42 μ g m⁻³ on December 3. 410 IF all of Ca _{anthropogenic} in the samples of other cities and cruises (Table 4) were calculated according to 411 same method, its level in this cruise was much higher than those in other samples, suggesting that 412 anthropogenic dust was dominated and distributed in the YRD region during the period.

Resembling Ca²⁺ distribution pattern, the maximum concentration and mass fraction of Na⁺ and K⁺ in 413 PM_{2.5} were also measured during EP-7. Significantly correlation between Ca²⁺ and K⁺ suggested that 414 415 dust could be the major source of K⁺ in PM_{2.5} sampled during YRC (Figure 3). In general, it's well known 416 that dust particles with the high alkalinity could firstly neutralize SO_4^{-1} and NO_3^{-1} in aerosol particles, then 417 atmospheric ammonia was absorbed. The concentrations and mass fractions of SNA in PM2.5 slightly 418 increased at the end of the cruise (Figure 3) since carbonate in aerosol could enhance the uptake of acidic 419 gases on particles (Huang et al., 2010). In the meanwhile, the increasing mass ratio of NO₃⁻/SO₄⁻ in EP-7 420 and EP-8 was attributed to two main reasons (Figure 3). The mobile sources (such as: vehicle emission) 421 increased and released a huge amount of NOx when the vessel was close to the megacity (Huang et al., 422 2013). Furthermore, NO_2 could transform into NO_3^{-1} via the heterogeneous process on dust aerosol 423 surface (Nie et al., 2012).

424 **3.4.3 Heavy metals in mega-city**

425 Heavy metals have toxic effects on plants, animals, and human beings. However, there is no uniform 426 stander concentration for control indicator (Sharma and Agrawal, 2005). The trace elements (component 427 3 and component 4), with highly EFs ranging from 24 to 1213, were considered to mainly come from 428 heavy oil and industry, respectively. The high concentrations of V and Ni were observed when the ship 429 berthed in the Waigaoqiao port berthing region of Shanghai (EP-8) (Figure 5b), where some field 430 observations have also identified that heavy oil combustion exert a significant impact on the local air 431 quality (Zhao et al., 2013b; Fu et al., 2014; Ding et al., 2017; Liu et al., 2017). It's also reported that the 432 transition metals of Ni and V were greatly enriched in smaller particles with a diameter of $< 1.0 \mu m$ (Jang 433 et al., 2007). Fine particle Ni (Figure 6i) had almost same spatial distribution with Cr (Figure 6j), that 434 Shanghai, Jiangsu, and the east of Anhui were identified as the major potential source regions and/or 435 pathways, owing to ship emissions, nonferrous metal mining, and smelting industries. The Mongolian plateau also was also a source region, indicating that nature dust may be possible source for Cr and Ni.
However, the high PSCF values of fine particle V were only derived from the YRD region and Mongolian
plateau (Figure 6j). It's partly that V was considered to originate from heavy oil combustion, while Ni
and Cr probably has other sources (Table S1) (Zhao et al., 2013b).

440 The temporal variations of component 4 peaked nearly in Wuhan and Shanghai (EP-4, EP-7, and EP-441 8) (Figure 5b) where China Baowu steel industry, and numerous shipyards were located in those regions 442 (Ivošević et al., 2016). Fine particle Fe, Co, Mn, and Zn displayed similar regional distribution (Figure 443 6l-o), and the high PSCF levels were observed in the YRD region, indicating that steel industries and 444 shipyards were densely distributed in East of Anhui, Jiangsu and Shanghai. Besides, the high PSCF value 445 for Zn (Figure 61) was also exhibited high value in Hubei, Henan, and Shanxi, probably due to the 446 influence of coal combustion and nonferrous metal smelting activities in these regions (Li et al., 2015b). 447 Overall, it should be noted that anthropogenic sources in mega-cities (WNS) were dominant origins for 448 trace elements in fine particles collected along this cruise.

449 **3.4.4 Biomass burning in rural region**

450 Numerous studies also have confirmed that levoglucosan mostly originate from biomass burning (Liang 451 et al., 2017; Ding et al., 2013b; Wan et al., 2017; Wang et al., 2014). The distribution of levoglucosan is 452 irregular parabolic from inland to coastal areas in Figure 3. The maximum value of levoglucosan (0.18 453 μ g m⁻³) was observed in the rural of Anhui province (EP-6), while its level in YRD region (EP-8) was at 454 very low levels. The elevated levels of CO and low-concentrations of SO₂ and NO_X also confirmed BB 455 in EP6 and EP7 (Table 2). However, fire points couldn't be apparently observed in the satellite-detected 456 fire maps (http://firefly.geog.umd.edu/firemap/), due to heavy cloud cover on 27 November and 1 457 December. During the whole observation periods, there was only one sample (#12, Figure S8) collected 458 during BB event. It was verified by MODIS fire points, due to a cold front blowing heavy clouds away 459 (Figure S4). The slightly higher levoglucosan concentration was observed in the night that was attributed 460 to the lower boundary layer at night and BB for heating and cooking in the rural regions.

461 The levoglucosan concentration and ratio of OC to lev (OC/lev) were also widely applied to estimate 462 the contribution of biomass burning to organic carbon in $PM_{2.5}$. To further quantify the contribution of 463 BB to OC, an empirical model was utilized as proposed by Wan et al. (2017):

464
$$OC_{BB} = \left(\frac{[lev]}{[OC]}\right)_{ambient} / \left(\frac{[lev]}{[OC]}\right)_{BB} (5)$$

465 The differences of the (lev/OC) BB ratio among different biomass fuels and combustion conditions were 466 taken into account. So, the average (lev/OC)_{BB} ratio of 8.14 % was selected to calculate the contribution 467 of BB to OC (Wan et al., 2017). Figure S9 presents the variation of lev/OC ratio along the Yangtze River. The ratio of lev/OC during this cruise ranged from 0.03 % to 0.91 % with an average of 0.35 \pm 0.24 %, 468 469 which was comparable to that of Lin'an in YRD region (Liang et al., 2017). However, the ratio of lev/OC 470 during YRC was near an order of magnitude of lower than its value in New Delhi $(3.1 \pm 0.8 \%)$ (Li et al., 471 2014) and Lumbini $(3.34 \pm 2.53 \%)$ in the northern edge of Indo-Gangetic Plain (Wan et al., 2017), where 472 BB play an important role on air quality. Figure S9 also shows the time serious of contribution of BB-473 OC to OC. The average contribution of BB-OC/OC was 4.26 ± 2.89 %, while the mean mass fraction of 474 OC to PM_{2.5} was slightly higher than 20%. The peak contribution of OC deriving from BB to total OC of 475 $PM_{2.5}$ nearly accounted for 11% in EP-6, which was approached that of the Pearl River region sites (13%) 476 (Ho et al., 2014). Here, it's emphasized that our method based on empirical formula and value is just 477 rough estimation. Hence, the radiocarbon measurement (¹⁴C) of carbonaceous aerosol and air quality 478 model simulation should need to confirm this result in the future.

479 **3.5 Ship emission**

480 **3.5.1 Primary of ship emission**

481 Over the past few decades, China's rapid economic development leads to the increasingly busy shipping 482 transportation in the Yangtze River. However, there is lack of data related to ship emission along the 483 stream of Yangtze River, especially in inland area. The ratio of V to Ni was used to judge whether ship 484 emission could influence air quality (Isakson et al., 2001). The average ratio of V/Ni in the cruise is 1.27, 485 which was in good agreement with the previous studies (Pandolfi et al., 2011; Zhang et al., 2014). 486 Emission factors of heavy metals from different types of fuel oil were also analyzed in our group (Table 487 S1). Only heavy oil contained V, while the V levels emitted from other diesel and petrol were under the 488 detector limits. In this study, only V was regarded as the tracer for heavy oil combustion. However, it 489 was still difficult to distinguish V from refinery and ship emission. Hence, the high-resolution back-490 trajectory, and high-resolution of the ship position from the AIS data were applied to investigate ship 491 plume during this cruise. As plotted in Figure 7, the numbers of the ship from AIS were closely related 492 to the V concentrations. From the inland region to the East China Sea at Shanghai, the concentration of V of PM_{2.5} generally increased, and reached the highest level of 0.06 μ g m⁻³ on 4 December when the 493

vessel berthed in the anchorage of the Yangtze River estuary. Meanwhile, air masses in this evening
originated from the port and anchorage (Figure S10). Hence, V of PM_{2.5} sampled in the port of Shanghai
could be probably attributable to ship emissions, especially from oceangoing vessels.

497 The contribution of primary ship emissions to $PM_{2.5}$ could be calculated by the equation developed by 498 Agrawal et al. (2009):

499
$$PM_a = \langle a \rangle \times \langle r \rangle \times V_a / \langle F_{V,HF0} \rangle$$
 (6)

where PM_a represents the primary PM_{2.5} concentration estimated (µg m⁻³); < a > is a coefficient of 500 the fraction of V from ship emissions in fine particles in China (0.85), $\langle r \rangle$ is average ratio of PM_{2.5} 501 502 to normalized V emitted (ppm); V_a represents the V amount of the samples ($\mu g m^{-3}$) during YRC, and 503 is the V content of heavy oil on average from the vessels (ppm). The value of < r > was set as 8205.8 504 ppm as Agrawal et al. (2009) reported. The value of $\langle F_{V,HFO} \rangle$ was set as 65.3 ppm, of which 505 represents of the average V contents (Zhao et al., 2013b). The average concentration of the primary ship 506 emission was $1.01 \pm 1.41 \ \mu g m^3$, ranging from 0.02 to 6.27 $\mu g m^3$, which is higher than that at Tuoji Island (0.65 μ g m⁻³) (Zhang et al., 2014). The peak level of primary ship emission was observed in the 507 508 Shanghai harbor.

509 **3.5.2 Ship emission contribution to SO_4^{2-}, NO_3^{-}, and OC**

To in-depth characterize the contribution of the ship emissions to secondary fine particles, a lower limit of the SO_4^{2}/V , NO_3/V , EC/V, and OC/V ratios (equal to the average minus one standard deviation) was applied to estimate the particulate from heavy oil combustion in the course of the Yangtze River (Becagli et al., 2017). As presented in Figure S11a-b, the mass ratio of SO_4^{2}/V and NO_3/V decreased rapidly with increasing V concentration. According to ship traffic numbers, weather condition, and the emission factors of different type oils (Table S1), the samples with V > 15 ng m⁻³ were mainly considered to come from ship emissions.

The limit ratio of SO_4^{2-}/V , NO_3^{-}/V and OC/V, and the estimation of ship emissions contributions to SO $^{2-}_4$, NO_3^{-} , OC, and $PM_{2.5}$ are summarized in Table S2 in supporting information. The minimum ratio of NO_3^{-}/V in this cruise was nearly twice greater than the limit ratio for SO_4^{2-}/V , which was contrary to the previous results with higher SO_4^{2-} from ship emissions observed in summer on the island of Lampedusa (35.5°N, 12.6°E) in the central Mediterranean. In general, SO_4^{2-} and NO_3^{-} in aerosol were mainly formed

522 through gas precursors of SO_2 and NO_X , respectively, both of which were completely different for lift-523 time and chemical processes in the atmosphere. High UV radiation and humidity could accurate the 524 reaction rate of SO₂ to SO₄² (Zhou et al., 2016). However, NO₃³ was in gas-aerosol equilibrium with 525 gaseous HNO₃(g). Low temperature and humidity would shift the gas-aerosol equilibrium to the particle 526 phase (NO₃) (Matthias et al., 2010; Wang et al., 2016). One reason for this discrepancy was probably 527 meteorological and photochemical conditions, which leaded to lower sulfur conversion rate, and 528 particulate NO₃ domination in the low temperature and moisture in winter during this cruise (Table 2). 529 On the other hand, NO₃ may have other sources in Shanghai port, whereas Lampedusa was a remote site 530 (Becagli et al., 2017). The average estimated concentration of minimum SO_4^2 derived from ship emission 531 was 1.38 μ g m⁻³ during YRC, which was similar to the value measured in the Mediterranean (Becagli et 532 al., 2017; Becagli, 2012).

533 EC and OC were also estimated by the same methods for SO_4^2 and NO_3 , and the lower limit for OC/V 534 and EC/V ratio are also presented in Figure S11c-d. Besides, the correlation of V with EC have a high value ($\mathbb{R}^2 = 0.71$, P < 0.01), suggesting that V and EC have same sources (Agrawal et al., 2009). In this 535 cruise, organic matter of PM_{2.5} were estimated from OC by multiplying a conversion factor of 1.4, due 536 537 to typical fresh emission and weak light in winter (Becagli et al., 2017). The estimated lower limit for 538 average of ship emissions was 7.65 µg m⁻³, nearly occupying 6.41% of PM_{2.5} during YRC. The peak ship 539 contribution could reach to 36.04% of total PM_{2.5} when the vessel berthed in the Waigaoqiao port of 540 Shanghai, which was slight above the value (20-30%) estimated by Liu et al. (2017) during ship-plume-541 influenced periods. It was noted that the ship emission decreased from Shanghai port to the inland area. 542 One reason for this was correspond to the density of ship in the Yangtze River channel. On the other 543 hand, fuel oils were completely different between the ship travelling in inland waterway and the 544 oceangoing vessel. In general, light diesel with low EFs of heavy metals (such as: V, Ni) was widely used 545 by the ships on river, whereas heavy oil showing high content of V and Ni were widely burned onboard 546 marine vessels as fuel (Table S1). Oceangoing ship emissions were probably major atmospheric pollution 547 sources in the Shanghai port. Hence, it is urgent to establish emission control areas (ECAs) in Shanghai 548 ports. However, it is worth noting that our estimation based on empirical values was also limited by 549 meteorological conditions and sample numbers. Hence, long-term observation and high resolutions 550 model simulation of ship emissions should be strengthened as part of control air quality along the Yangtze 551 River, especially in Shanghai harbor cluster.

553 In order to better characterize air quality over the region of MLYR, an intensive atmospheric observation 554 was conducted during YRC. A ship-suit measurements was used to characterize an suite of air pollutants 555 (trace gases and fine particles) in this region. The average concentrations of $PM_{1.0}$ and $PM_{2.5}$ were 96.69 \pm 22.18 µg m⁻³ and 119.29 \pm 33.67 µg m⁻³ during the cruise, respectively. The most abundant species in 556 557 $PM_{2.5}$ was $SO_4^{2.5}$ with an average concentration of 15.21 ± 6.69 µg/m³, followed by NO₃⁻ (13.76 ± 4.99 μ g/m³), NH₄⁺ (9.38 ± 4.35 μ g/m³), Ca²⁺ (2.23 ± 1.24 μ g/m³), respectively. Combined with satellite 558 559 data, back trajectory, principal component analysis (PCA), and potential source contribution functions 560 (PSCF), major chemical composition of PM_{2.5} manifested greatly geographical differences and diverse 561 anthropogenic emission sources from coastal to inland regions. Wuhan suffered secondary aerosol 562 pollution with SNA accounting for nearly 50% of PM_{2.5}. The significant correlation between Se and SO 563 ²⁻ revealed that the stationary emissions may play an important role in SNA formation. The concentrations 564 of levoglucosan of PM_{2.5} and CO column levels from the satellite data significantly enhanced in the rural 565 areas (Anhui and Jiangxi), indicating that BB from the both shores of the Yangtze River may make 566 remarkable contribution to air pollution in this area during YRC. Further, the crustal elements of Al and Ca presented the high levels in the YRD regions and the high value of enrichment factors (EFs) of Ca 567 568 (EFs > 100) coupling with the PSCF results suggested the crustal elements may derive from re-569 suspension of dust from road and/or construction activity along the banks of the Yangtze River. Ship 570 emissions displayed a significant effect on air pollution, and could contribute to more than 36% of PM_{2.5} 571 in the ports of Shanghai. As far as we know, it's the first comprehensive observation of air quality over 572 the MLYR region using a vessel mobile platform. The results herein suggested that the differentiated 573 control measures in accordance with local pollution characteristics should be taken to tackle air pollution.

- 574 **Competing interests**
- 575 The authors claim that they have no competing interests.
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Captions of Figure and Table

Table 1. The detailed information of PM_{2.5} and PM_{1.0} in the ambient during YRC.

Table 2. The pollutant levels and meteorological parameters in eight different episodes.

Table 3. The average concentration of the elements in PM_{2.5} and PM_{1.0} (ng m⁻³) during YRC

Table 4. Comparisons of trace element concentrations with the reported data ($\mu g m^{-3}$).

Figure 1. Cruise tracks, source region limits, the sampling sites, and land use during YRC.

Figure 2. The average distribution of (a) aerosol optical depth at 550nm (MODIS L2); (b) CO column mixture ratio (MOPITT L2); (c) the SO₂ column concentration (OMI L2); (d) the NO₂ column concentration (OMI L2) over MLYR region.

Figure 3. Spatial concentration distributions of the soluble ions and levoglucosan in $PM_{2.5}$ along the cruise path.

Figure 4. Comparisons major ionic species during YRC with other regions, including: Beijing, Xi'an, Chengdu, Wuhan, Guangzhou, Shanghai, Northern South China Sea, Taiwan Strait, South China Sea, East China Sea and Tuoji Island. The red lines mark the sample routes in different cruises.

Figure 5. (a) Principal component analysis (PCA) of the typical elements in $PM_{2.5}$; (b) Time series of four typical element sources derived from PCA. All of the units are in $\mu g m^{-3}$.

Figure 6. Probable sources from PSCF for individual elements in PM_{2.5} during YRC. The criteria are the mean concentration for all.

Figure 7. Time serious of V concentration (read column), estimates of primary PM_{2.5} from ship emission, and number of ship distribution in the Yangtze River channel during YRC.

Sample Number	Start data UTC	Day/Night Samples	Ship state	Sampling duration	Average Latitude, °N	Average Longitude, °E	PM2.5 (μg m ⁻³) I	PM _{1.0} (μg m ⁻³)	PM1.0/PM2.5
#1	25-Nov-15	Daily	Moving	24 hours	30.95	117.78	63.83	58.30	91.33%
#2	26-Nov-15	Daily	Moving	24 hours	30.30	116.95	112.70	84.58	75.06%
#3	27-Nov-15	Daily	Moving	24 hours	29.73	115.86	106.40	90.37	84.96%
#4	28-Nov-15	Daily	Moving	24 hours	30.37	115.06	81.49	73.69	90.43%
#5	29-Nov-15	Daytime	Moving	12 hours	30.63	114.53	157.70	136.10	86.32%
9#	29-Nov-15	Nighttime	Stopping	12 hours	30.69	114.45	161.80	152.20	94.06%
L#	30-Nov-15	Daytime	Moving	12 hours	30.42	114.92	80.56	65.56	81.38%
#8	30-Nov-15	Nighttime	Stopping	12 hours	30.09	115.32	106.30	89.29	83.99%
6#	1-Dec-15	Daytime	Moving	12 hours	29.72	115.97	96.00	81.83	85.24%
#10	1-Dec-15	Nighttime	Moving	12 hours	30.32	116.89	92.02	82.86	90.04%
#11	2-Dec-15	Daytime	Moving	12 hours	31.08	117.96	122.80	85.17	69.34%
#12	2-Dec-15	Nighttime	Moving	12 hours	31.90	118.55	163.20	118.40	72.55%
#13	3-Dec-15	Daytime	Moving	12 hours	32.27	119.44	152.90	108.70	71.09%
#14	3-Dec-15	Nighttime	Moving	12 hours	31.95	120.27	133.90	105.60	78.89%
#15	4-Dec-15	Daytime	Moving	12 hours	31.70	121.18	146.10	111.80	76.57%
#16	4-Dec-15	Nighttime	Stopping	12 hours	31.38	121.60	131.20	102.70	78.27%

Table 1

Periods	Data and time (BST ^a)	Latitude	Longitude	wind speed (m/s)	RH%	NOX (ppb)	SO ₂ (ppb)	CO (ppb)	PM 2.5 (SN ^b)	T/B
EP-1	2015/11/22 12:00 to 2015/11/23 18:00	31.28 to 32.22	121.23 to 119.55	3.01	88.95	65.51	6.32	443.91		1.59
EP-2	2015/11/25 12:00 to 2015/11/27 14:00	31.01 to 29.91	117.79 to 116.35	2.86	66.73	57.50	12.45	704.48	(#1,2)	0.81
EP-3	2015/11/27 14:00 to 2015/11/29 00:00	29.84 to 30.50	116.35 to 114.83	2.48	69.72	68.16	16.15	676.20	(#3,4)	1.49
EP-4	2015/11/29 00:00 to 2015/11/30 18:00	30.50 to 30.18	114.83 to 115.25	2.18	83.01	62.65	8.60	1030.25	(#5-7)	0.97
EP-5	2015/11/30 18:00 to 2015/12/01 20:00	30.18 to 30.02	115.25 to 116.66	2.32	79.64	51.92	11.66	989.75	(#8,9)	2.61
EP-6	2015/12/01 20:00 to 2015/12/02 20:00	30.02 to 31.67	116.66 to 118.40	3.84	74.67	31.00	4.09	1139.33	(10,11)	0.96
EP-7	2015/12/02 20:00 to 2015/12/03 20:00	31.67 to 32.32	118.40 to 119.73	5.39	44.91	23.73	7.87	1224.88	(#12,13)	1.00
EP-8	2015/12/03 20:00 to 2015/12/05 06:00	32.32 to 31.36	119.73 to 121.61	2.68	38.86	57.55	16.62	1061.46	(#14-16)	1.73

^a Beijing standard time (GMT-8); T/B is ratio of toluene to benzene; ^b sample number in Table 1.

Table 2

Contents		Average	Max	Min	Median	SD^{a}
M~	PM _{2.5}	629.87	1487.67	135.69	589.13	358.57
Mg	PM _{1.0}	328.57	699.09	17.26	359.42	213.44
A 1	PM _{2.5}	863.87	2400.13	21.13	786.17	618.66
Al	$PM_{1.0}$	631.37	1894.40	100.78	473.46	483.74
V	PM _{2.5}	865.88	1723.87	368.51	805.73	367.14
K	$PM_{1.0}$	771.80	1560.67	326.41	739.86	303.33
Ca	PM _{2.5}	2724.35	5657.60	391.54	2381.94	1729.51
Ca	$PM_{1.0}$	1525.39	3371.73	108.21	1455.19	1108.03
V	PM _{2.5}	9.71	60.00	0.19	7.33	13.45
v	$PM_{1.0}$	9.20	55.50	1.18	6.80	12.72
C.	PM _{2.5}	22.29	62.67	2.16	16.73	16.51
Cr	$PM_{1.0}$	21.67	48.17	2.67	22.74	13.31
Ma	PM _{2.5}	56.63	152.12	9.08	42.56	43.42
MIN	PM _{1.0}	45.80	106.33	8.58	31.56	31.75
E-	PM _{2.5}	1644.84	5188.18	38.87	860.40	1590.29
Fe	PM _{1.0}	934.30	2616.83	46.74	516.37	850.12
Ca	PM _{2.5}	0.82	2.88	0.00	0.48	0.75
Co	PM _{1.0}	0.62	1.67	0.07	0.26	0.53
NT:	PM _{2.5}	10.53	73.64	1.83	5.61	16.82
IN1	PM _{1.0}	8.19	32.29	1.39	4.35	7.89
Cu	PM _{2.5}	18.79	49.87	4.07	17.66	11.28
Cu	PM _{1.0}	15.21	37.07	3.70	12.32	7.87
7	PM _{2.5}	295.08	638.08	125.36	221.83	159.05
Zn	PM _{1.0}	288.84	485.26	81.91	261.06	156.34
Åc	PM _{2.5}	37.33	107.17	0.87	31.50	28.14
AS	PM _{1.0}	41.73	111.85	12.46	30.70	32.00
Sa	PM _{2.5}	6.08	12.18	2.70	5.78	2.57
56	$PM_{1.0}$	6.48	11.04	3.07	6.40	2.76
Cł	PM _{2.5}	2.72	5.00	1.30	2.50	1.06
	PM _{1.0}	5.42	39.20	1.30	3.33	9.09
	PM _{2.5}	0.32	0.90	0.00	0.29	0.22
11	PM _{1.0}	0.41	0.89	0.14	0.35	0.23
DL	PM _{2.5}	98.37	176.54	53.26	95.68	35.91
PD	PM _{1.0}	110.45	274.80	53.04	102.84	54.07

Table 3

^aSD is one standard deviation.

	2015 ^a	2003	2011	2013-2014	2012-2013	2011	2012-2013	2008-2009	2009-2010
	(this study)	(Zhang et al., 2007)	(Zhao et al., 2015)	(Li et al., 2016)	(Lai et al., 2016)	(Tao et al., 2014)	(Zhang et al., 2015)	(Huang et al., 2013)	(Zhao et al., 2013)
	Winter	Spring	Spring	Winter	Winter	Winter	Winter	Winter	Winter
	Yangtze <mark>River</mark> channel ^b	Northern South China Sea	East China sea	Taiwan strait	Guangzhou (rural)	Chengdu	Wuhan	Shanghai	Beijing
AI	0.86	0.31	3.28	3.00	0.21	0.43	I	0.64	1.03
Ca	2.72	0.82	2.40	2.00	0.11	0.26	2.27	0.72	1.85
Fe	1.64	0.32	1.37	1.30	0.16	0.61	1.42	0.56	1.55
Mg	0.63	0.11	0.83	2.40	2.30	0.16	0.61	0.26	0.57
\mathbf{As}	0.04	I	0.01	I	I	0.02	0.04	0.02	0.01
Cd	0.00	I	I	I	I	0.00	0.01	I	I
Cr	0.02	0.03	I	0.60	I	0.01	0.01	0.02	0.01
Cu	0.02	I	0.01	I	0.03	0.03	0.03	0.04	0.04
Mn	0.06	I	0.01	0.70	0.03	0.07	0.13	0.04	0.09
Ni	0.01	I	0.01	06.0	I	0.00	0.01	0.01	0.01
Pb	0.10	0.16	0.02	0.70	0.09	0.20	0.24	0.06	0.15
Λ	0.01	I	0.02	I	I	0.00	I	0.01	I
Zn	0.30	I	0.07	0.60	0.27	0.32	0.37	0.13	0.30
^a Sampling pe	riods; ^b Samplir	ıg sites							

Table 4

Figure 1.



Figure 2.



Figure 3.



Figure 4.



Figure 5.





Figure 6.



Figure 7.



Supporting information:

Air quality in the middle and lower reaches of the Yangtze River channel: A cruise campaign

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1 Meteorology pattern over the cruise

The MLYP region is located in East Asia Monsoon Region (China type), of which has a clear seasonal shift of the prevailing wind between in winter and summer. As shown in Figure S3, West Pacific Subtropical High (WPSH) control the south China in winter, while a cold high pressure formed in the north region of China during the period. During the sampling periods, WPSH was constantly squeezed further to south and ocean. The YRC region is completely situated between high pressure ridge and trough, thus northwest winds are dominant, as verified by two cold fronts on 25 November and 2 December in 2015, respectively. Besides, a low-pressure system formed in central China from 28 to 30 November, which was characterized by relative low wind speed and even stagnant air-mass, of which made a great contribution to the formation of the haze pollution (Huang et al., 2014;Huang et al., 2012).

The detailed meteorological information, including temperature (T), RH, pressure, wind speed (WS) and wind direction (WD) were monitored by an automatic meteorological station (HydroMetTM, Vaisala) placed on the front of the vessel. The true wind, i.e., a vector wind with a speed referenced to the fixed earth and a direction referenced to true north, was established by the platform-relative wind to ship and vessel speed, which was calculated directly from Global Positioning System (GPS) records (Smith et al., 1999). T and RH showed greatly changes during the survey, range from 1.05-18.90 °C and 26.90-99.00%, respectively. The surface WD was relative constant and WS was low in the most time during YRC, and the mean speed of 3.10 ± 0.99 m/s were measured. There were two sharp reduction of T and RH on 25 November and 2 December. When the cold front arrived, WS increases from 2 m/s up to 10 m/s.

Table S1. Emission factors of 11 metals from different fuel combustion (mg/kg) measured in our lab
(Wu et al., 2017).

	Light diesel oil	Marine heavy oil	93 octane petrol	97 octane petrol
As	7.91 ± 1.03	1.77 ± 0.51	2.55 ± 0.31	1.30 ± 0.17
Fe	7.87 ± 1.12	12.28 ± 2.85	18.30 ± 1.39	20.07 ± 0.48
Al	4.39 ± 1.26	1.25 ± 0.35	0.33 ± 0.00	0.21 ± 0.00
Mn	2.62 ± 0.45	2.47 ± 0.70	0.57 ± 0.24	0.41 ± 0.03
Pb	1.13 ± 0.15	12.39 ± 0.65	ND	ND
Cr	0.73 ± 0.08	0.22 ± 0.09	0.24 ± 0.05	0.16 ± 0.10
Zn	0.43 ± 0.05	5.46 ± 1.32	0.05 ± 0.02	0.09 ± 0.03
Cu	0.40 ± 0.16	0.10 ± 0.03	0.40 ± 0.00	0.27 ± 0.12
V	ND	0.48 ± 0.11	ND	ND
Cd	ND	ND	ND	ND
Ni	0.24 ± 0.02	0.39 ± 0.06	0.07 ± 0.01	0.21 ± 0.04
TMs	25.72 ± 4.32	36.81 ± 6.67	22.51 ± 2.02	22.72 ± 0.97

Table S2. The average and maximum contribution of SO_4^{2-} , NO_3^{-} , OC and $PM_{2.5}$ from ship plume estimated by a lower limit ratio.

Ship emission contribution	PM2.5	$(OM/V)_{min} = 290$	(NO_3/V) min = 228	$(SO_4^2/V) min = 127$
Average (µg m ⁻³)	7.66	2.82	2.22	1.38
Maximum (µg m-³)	47.23	17.40	13.8	8.55



Figure S1. Ship route and 3-day back trajectories arriving at 500 m above sea level.



Figure S2. Time series of (a) meteorological parameters during YRC (T and RH); (b) ratio of

Toluene to Benzene.

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Figure S3. The average geopotential height field (white lines) and wind field (blank vector) for 750 hPa for each day during YRC.



Figure S4. MODIS true-color imagery on 28 November, 2 and 3 December in 2015.



Figure S5. (a) The ion balance; (b) The correlation between the equivalent concentrations of $[SO_4^{2-} + NO_3^{-}]$ and $[NH_4^+ + Ca^{2+}]$ in the present study (μ eq m⁻³).



Figure S6. (a) average mass concentration of the main soluble ions along YRC; (b) the linear correlation between Se and SO_4^{2-} in PM_{2.5}.



Figure S7. Residential coal consumption in China in 2015 (source: China energy statistical yearbook (NBSC, 2016)).



Figure S8. Mean wind vectors for sample #12 beginning at 18:00 LST and ending at 06:00 LST next day. Green line is the route for this sample. Red dots represent the FIRMS's fire points.



Figure S9. Time serious of Lev/OC and Lev/ $PM_{2.5}$ ratios, and contribution of BB-OC to OC and $PM_{2.5}$ during YRC



Figure S10. 18-hours back trajectories arriving at 500 m above sea level during the sample #16.



Figure S11. Scatter ration of (a) SO_4^{2-}/V , (b) NO_3^{-}/V , (c) EC/V and (d) OC/V along YRC. The red dashed line represented average ratio and solid line express the minimum ratio (average minus one standard deviation) for the sample with V > 15 ng/m³.

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