Anonymous Referee #1

This manuscript investigates atmospheric new particle formation in a polluted marine environment. The paper addresses on important topic and reports on observations that are original enough for a scientific publication. The analysis conducted in the paper has, however, a few weaknesses that require more work before I can recommend publication. The detailed comments are given below.

Response: We thank this reviewer's comments. In this manuscript, we investigate new particle formation events in polluted marine atmosphere in different extents and evaluate their potential climatic impacts. We agree that some issues presented in this manuscript are not well justified and needed to be improved. Moreover, the weaknesses of CMAQ should also be considered in interpreting those events. We thereby revise our manuscript according to these constructive comments.

Main issues

The authors motivate their research with the potential connection between marine new particle formation, CCN production and climate (CLAW hypothesis). The problem with this approach is that the CLAW hypothesis can only be investigated in a remote marine environment where the anthropogenic influence is minor. The investigation of this paper has been made in a polluted marine environment and, as also the authors state in there paper, the observed new particle formation events seem to be associated with continental pollution. The character of marine new particle formation is very different between the remote marine boundary, polluted marine air, and some coastal environments such as Mace Head. The authors should make a clear difference between these different marine environments and put their investigations into a correct context. The same should also be kept in mind when analyzing the results (e.g. section 3.1).

Response: As presented in our manuscript, most of new particle formation events in polluted marine atmosphere were likely associated with anthropogenic pollutants. A few weak new particle events could be associated with ocean-derived gases, but we cannot exclude the contribution from anthropogenic pollutants. The polluted marine atmosphere is indeed not an ideal place to argue CLAW hypothesis. Thus, the part will be revised as "Oceans account for approximately 70% of areas on the earth. Huge efforts have been taken to improve understanding of the relationship between production of new particles in marine atmosphere and their impacts on the climate in the last three decades (Charlson et al., 1987; O'Dowd et al., 2007; Quinn and Bates, 2011). Several earlier studies focused on new particle formation (NPF) in remote marine atmosphere and some clear coastal environments such as Mace Head, where dimethylsulfide (DMS) and iodine have been proposed to be important precursors for new particles (Cover et al., 1996; Clarke et al, 1998; O'Dowd et al., 2002; O'Dowd et al., 2007; Chang et al., 2011). In polluted marine atmosphere, high concentrations of secondary particulate species generated from anthropogenic and/or biogenic precursors as well as a small amount of particulate methanesulfonic acid from marine

biogenic sources were frequently observed and these observed species were proposed to have important impacts on regional climate (Yang et al., 2009; Shi et al., 2010; Feng et al., 2012; Wang et al., 2014). For indirect climate effects, the number concentration of atmospheric particles is critical. However, direct measurements of NPF events are still limited and the same can be said for assessing their potential contribution to CCN (Lin et al., 2007). In addition, the characters of NPF among in polluted, remote marine and clear coastal environments could be very different. Thus, more observations for NPF events in polluted marine atmosphere are essential.

To improve understanding the characters of NPF events in polluted marine atmosphere in different extents and evaluating their potential climatic impacts, we investigated NPF and their subsequent growth in the marginal seas of China including the Yellow Sea and the East China Sea during two cruise campaigns from 16 October to 5 November 2011 and from 2 to 11 November 2012."

The paper does not define its scientific goals properly. It is only stated that "to improve understanding on these issues…" (line 22 on page 3045). Which issues? What are the concrete scientific questions this study aims to answer?

Response: See response above.

The causes for new particle formation and growth (sections 4.1 and 4.2) have been analyzed solely based on the CMAQ model results. This is problematic for several reasons. First, CMAQ does not include marine aerosol precursor emissions. Second, CMAQ simulates PM2.5 mass, but neither the particle number size distribution nor the distribution of chemical species over different particle sizes. Third, there is no separation between SOA of different volatility in CMAQ. Because of this, CMAQ simulation results are only indicative of causes of new particle formation and growth and should be interpreted with extreme care. For example, the presence of ammonium nitrate or SOA in PM2.5 does not guarantee that the same species would contribute to new particle formation and growth. Several studies indicate that semi-volatile SOA is very inefficient in growing newly-formed particles (see Riipinen et al. 2011; Ehn et al. Nature 2014).

Response: The weaknesses of CMAQ modeling results will be highlighted in the revision and also in the support information, such as the treatment methods of particle size distribution and different volatile SOA in CMAQ v4.7.1. In interpreting our observed formation and growth of new particles, these weaknesses will be carefully considered in different sections. We also soften our conclusion accordingly. Please see our revised version.

Minor/technical issues:
Lines 4-14 on page 3045: The authors might consider citing the recent overview by Kerminen et al. (2012, Atmos Chem Phys 12, p. 12037) on CCN production

associated with atmospheric nucleation here.

Response: We are sorry to miss the important reference and will add it in the revision.

Past tense should be preferred in sentences like to in line 6 of page 3046, and lines 9-10 of page 3047. Please check out throughout the text.

Response: Agree. We will correct the grammatical errors throughout the text in the revision. Please see our revised version.

I do not understand the first sentence of section 4.1. Is this a general statement? If yes, then a present tense rather than past one is needed.

Response: A present tense will be used in the revision.

Page 3056, line 2: "much low mixing ratio", improper wording.

Response: The sentence is indeed not accurate. In the revision, the part will be corrected as "Ambient sulfuric acid gas (H_2SO_4) has been reported to yield a negligible contribution to condensational growth of >10 nm new particles (e.g., 2% of the GR of 7-20nm particles, Riipinen et al., 2011; Ahlm et al., 2012; Pierce et al., 2012). This could be also true in the marine atmosphere of the marginal seas of China where the modeling mixing ratios of H_2SO_4 were less than 2 ppt during all NPF events".

Page 3056, line 6: 3 ppb does not sound a very low SO2 concentration to me. In many continental locations, there is plenty of gaseous sulfuric acid even at much lower SO2 levels. It is the balance between sulfuric acid sources and sinks that determine its concentration, not just the SO2 concentration.

Response: Agree. In the revision, the part will be corrected as "Ambient sulfuric acid gas (H_2SO_4) has been reported to yield a negligible contribution to condensational growth of >10 nm new particles (e.g., 2% of the GR of 7-20nm particles, Riipinen et al., 2011; Ahlm et al., 2012; Pierce et al., 2012). This could be also true in the marine atmosphere of the marginal seas of China where the modeling mixing ratios of H_2SO_4 were less than 2 ppt during all NPF events".

I am not convinced about the particle shrinkage discussed on pages 3051 (line 1) and 3056 (lines 14-22). Are the authors sure that the observation represents particle shrinkage? It might also be due to slight changes in measured air masses, especially and the new particle formation and growth seems to take place in a plume of continental outflow. Furthermore, it is definitely not only the Kelvin effect that matters in partitioning SOA between particles of different size (e.g. Riipinen et al. 2011), as

claimed on lines 14-22 on page 3056.

Response: We first reported particle shrinkage in Hong Kong using SMPS with 5-min time resolution (Yao et al., AST, 2010) and particle shrinkage was also observed by SMPS using 7-min time resolution (Young et al., ACP, 2013). In these low time resolution measurements, the decreasing size of new particles could be due to particle shrinkage and it could also be due to slight changes of measured air mass as this reviewer suggested. However, in this study, the time resolution of FMPS is as high as 1s. Any slight change will cause rapid response of $D_{pg,1}$ and $N_{<30nm}$ (Figs 2-6). The smooth and long time decrease of $D_{pg,1}$ and $N_{<30nm}$ was less likely related to changes of air mass, although we cannot completely exclude the possibility. In the revision, we will add "This phenomenon could also be related to slight changes of measured air mass, but the influence should be minor. Since the time resolution of FMPS was as high as 1 s, rapid responses of $D_{pg,1}$ and $N_{<30nm}$ corresponding to slight changes of air mass can be detected, e.g., $D_{pg,1}$ and $N_{<30nm}$ fluctuated dramatically during 14:00-17:00LT on 18 October 2011 (Fig. 4). However, the $D_{pg,1}$ and $N_{<30nm}$ after 13:30LT on Day 5 decreased smoothly for one and half hours."

Moreover, due to the interference from ship emissions, the decrease of $D_{pg,1}$ at 16:44 to 34 nm at 17:25 on 4 November 2012 could be due to particle shrinkage or due to slight changes of air mass. Thus, the later possibility will be added "However, it also could be due to the change in measured air mass." in the revision.

We agree not only the Kelvin effect that matters in partitioning SOA between particles of different size. In the revision, the part will be revised as "The coexistence of the shrinkage of new particles and the growth of particles (> 50 nm) were never reported in literature. Riipinen et al (2011) and Ehn et al (2014) recently reported that SOA condensation was a combination of kinetic condensation and thermodynamically partitioning of vapors on aerosol surface area. Kinetic condensation cannot explain the shrinkage from 21 nm to 17 nm. The possible explanation for the coexistence phenomenon was that the shrinkage of new particles was likely due to the Kelvin effect (Zhang et al., 2012); while particles (> 50 nm) were less affected by the Kelvin effect and they can grow to CCN size by condensation of species with relatively moderate or high volatility. However, more studies are needed to examine whether the coexistence phenomenon frequently occurs in polluted marine atmosphere and what caused it."

Dr. Chen (Referee)
jmchen@fudan.edu.cn

Line 22, Page 6 and Lin 13, Page 7, "on the ship" could be "on board".

Response: Corrected in the revision. Please see our revised version.

Line 10, Page 9, "twice times of the" should be "twice of the".

Response: Corrected in the revision. Please see our revised version.

Lines 7-8, Page 10, please check "A longer NPF event was observed from 10:30 on Day 2 to 03:50 LT on 18 October 2011 (Day 3)", it looks like the second NPF event was from 10:30 to 11:40 (check your exact time) on Day 2 (Fig. 3a and b), the bottleneck of about 30 nm at 11:40 on Day 2. If so, the consequent growth rate and discussion should be changed.

Response: At the 11:35LT on 17 October 2011, the number concentration of new particles reached the maximum value. This will be highlighted in the revision. The number concentration started to decrease after 11:35LT, but new particles continuously grew. The growth rate of new particles indeed decreased slightly after 11:40LT, which could be due to decreasing formation rate of non-volatile SOA (Fig S7 in supporting information). We believe the NPF event observed from 10:30 on Day 2 to 03:50 LT on 18 October 2011 should be considered as a long NPF event with varying growth rate of new particles rather than two NPF events.

List of what we changed in the revised version of manuscript:

Original	Revised
Page 3043, author names and institutional address	**Line 3**: change "X.H. Yao[1]" to "X.H. Yao[1,3]" **Line 9**: add the second institutional address of X.H. Yao
Page3044, after line 18	**Line 30-32**: add the limitation of CMAQ "However, the findings were obtained from the limited data and the simulations of CMAQ also suffered from several weaknesses such as only having three size bins for different particles, lack of marine aerosol precursors, etc."
Page3045,line12	**Line56**: cite the paper of Kerminen et al., 2012
Page3045,line18-22	**Line 63-78**: according to the comment of Anonymous Referee #1, "The authors should make a clear difference between these different marine environments and put their investigations into a correct context.", we add the difference between different environment.
Page3045, line22	**Line79-80**, we clarify the scientific goals of this study
Page3046,line2	**Line89**: change "interpret these NPF events" to "interpret these events"
Page3046,line6	**Line 94**: change "two cruise campaigns have been organized" to "two cruise campaigns were organized"
Page3046,line8	**Line96**: change "The two campaigns are to provide services" to "The two campaigns were to provide services"
Page3047,line9	**Line122**: change "Particles size distributions in this study are not uni-modal" to "Particles size distributions in this study were not uni-modal"
Page3047,line10	**Line123**: change "they are dominated by" to "they were dominated by"
Page3047,line12	**Line125**: change "which was expressed mathematically" to "which is expressed mathematically"
Page3048,line14	**Line152-157**: we add treatment methods of particle size distribution and SOA simulation in CMAQ model
Page3048,line18	**Line161**: cite the paper "Kulmala et al., 2013"
Page3048,line22 Page3049,line12	**Line165 and line182**: change "on the ship" to "on board" according comment of Referee #2
Page3049,line17	**Line 187**: change "in the daytime on 4 November" to "in the daytime of 4 November"
Page3050,line5	**Line201**: we change "two events were all within the range" to "two events are all within the range"
Page3050,line9-11	**Line205-207:** change the sentence "Based on the new particle growth 10 curves shown in Fig. S2a, the growth curve in the Yellow Sea after 09:30 LT almost paralleled to that at OUC" to "The new particle growth curves show that the curve in the

	Yellow Sea after 09:30LT almost parallels to that at OUC (Fig. S2a)"
Page3050, line15	**Line 211**: change "This suggested that" to "These suggested that"
Page3050,line17-18	**Line214**: change "These higher $N_{<30nm}$ values in the Yellow Sea" to "However, these values in the Yellow Sea"
Page3050, line25	**Line221**: change "which was close to the growth rate" to "which is close to the growth rate"
Page3051, line2	**Line225**: add "However, it also could be due to the change in measured air mass" after "(Yao et al., 2010; Young et al., 2013)" according the comment of Anonymous Referee #1
Page3051, line10	**Line234**: we change "the value was almost twice times of the first-phase growth rate " to "the value was almost twice of the first-phase growth rate"
Page3051,line13-14	**Line238**: change "growth rates of nucleated particles have been reported to be" to "growth rates of nucleated particles were reported to be"
Page 3052,line 11	**Line265**: add "during the period 10:30 to 11:35LT" after "4.1 particles cm^{-3} s^{-1}"
Page3052,line24	**Line 278**: change "see Supplement for the approach" to "see supporting information for the approach"
Page3053,line24	**Line306**:add "apparently" before "shrank down to 17 nm"
Page3053, line26	**Line 308-314**: add "This phenomenon could also be related to slight changes of measured air mass, but the influence should be minor. Since the time resolution of FMPS was as high as 1 s, rapid responses of $D_{pg,\ 1}$ and $N_{<30nm}$ corresponding to slight changes of air mass can be detected, e.g., $D_{pg,\ 1}$ and $N_{<30nm}$ fluctuated dramatically during 14:00-17:00LT on 18 October 2011 (Fig. 4). However, the $D_{pg,\ 1}$ and $N_{<30nm}$ after 13:30LT on Day 5 decreased smoothly for one and half hours." After "Young et al., 2013)."
Page 3054,line6-7	**Line321**: we change "the apparent formation rate of new particles was 1.4 particles cm^{-3} s^{-1} of the first short event, while the rate increased up to 3.1 particles cm^{-3} s^{-1} in the second event" to "the apparent formation rate of new particles is 1.4 particles cm^{-3} s^{-1} of the first short event, while the rate increase up to 3.1 particles cm^{-3} s^{-1} in the second event".
Page3054,line16	**Line331**: add "Fig. S5a" after "Fig. 2c".
Page3054,line17	**Line332**: add "apparently" before "supported our postulation"
Page3055,line3	**Line345**: change "Fig. S5" to "Fig. S6"
Page3055,line8	**Line350**: add "(Fig. 6, Fig. S5e)" after "10:00LT"
Page3055,line9	**Line 351**: change "but there are " to "but there is"
Page3055,line13	**Line356**: change "chlorophyll a data suffered from" to "chlorophyll a data suffer from"

Page3055,line20	**Line363**: add "Fig. S5b and 7b" after "(Fig. 3c)"
Page3056,line2-6	**Line374-378**: change "Due to much low mixing ratio of sulfuric acid gas in the atmosphere, sulfuric acid gas has been reported to yield a negligible contribution to condensational growth of > 10nm new particles (Pierce et al., 2012; Ahlm et al.,2012). This could be also true in the marine atmosphere of the marginal seas of China where the modeling mixing ratios of SO_2 were less than 3 ppb during all NPF events" to "Ambient sulfuric acid gas (H_2SO_4) has been reported to yield a negligible contribution to condensational growth of >10 nm new particles (e.g., 2% of the GR of 7-20nm particles, Riipinen et al., 2011; Ahlm et al., 2012; Pierce et al., 2012). This could be also true in the marine atmosphere of the marginal seas of China where the modeling mixing ratios of H_2SO_4 were less than 2 ppt during all NPF events"
Page3056,line 7-8	**Line380**: change "Pierce et al., 2012;Riipinen et al., 2011" to "Riipinen et al., 2011; Pierce et al., 2012"
Page3056,line 9	**Line 381**:change "secondary organics aerosol" to "SOA"
Page3056,line16	**Line 388-389**: add "(Fig. 6c and Fig. S7e)" after "a decrease of SOA in mass concentration"
Page3056,line17	**Line 389**: we add "(Fig. S4)" after "still grew at that period"
Page3056,line17-22	**Line389-400**: change "The coexistence of the shrinkage of new particles and the growth of particles (> 50 nm) suggested that semi-volatile SOA determined both processes. The coexistence phenomenon also suggested that the shrinkage of new particles was likely due to the Kelvin effect (Zhang et al., 2012), but particles (> 50 nm) were less affected by the Kelvin effect and they can grow to CCN size by condensation of species with relatively high volatility" to "The coexistence of the shrinkage of new particles and the growth of particles (> 50 nm) were never reported in literature. Riipinen et al (2011) and Ehn et al (2014) recently reported that SOA condensation was a combination of kinetic condensation and thermodynamically partitioning of vapors on aerosol surface area. Kinetic condensation cannot explain the shrinkage from 21 nm to 17 nm. The possible explanation for the coexistence phenomenon was that the shrinkage of new particles was likely due to the Kelvin effect (Zhang et al., 2012); while particles (> 50 nm) were less affected by the Kelvin effect and they can grow to CCN size by condensation of species with relatively moderate or high volatility. However, more studies are needed to examine whether the coexistence phenomenon frequently occurs in polluted marine atmosphere and what caused it."
Page3056,line27	**Line406**: change "indicating the contribution of SOA" to

	"suggesting the contribution of SOA"
Page3057,line3	**Line411**: change "Day 1 and Day 2 may be one factor" to "Day 1 and Day 2 might be one factor"
Page3057,line5	**Line414-417**: add "The modeling results showed that formation of NH_4NO_3 indeed occurred in $PM_{0.1}$ (Fig. S5a and b) and $PM_{2.5}$ (Fig. 2c and 3c) on Day 1 and Day 2, however, we cannot confirm whether NH_4NO_3 were formed on 30-40 nm particles due to the limitation of CMAQ" after "growth limit of 30-40 nm"
Page3057,line14	**Line427**: change "The maximum diameter of new particles" to "The maximum diameters of new particles"
Page3057,line18	**Line432**: change "The modeling results indicated that" to "The modeling results suggested that"
Page3057,line19-20	**Line433**: change "when SO_2 showed obviously low concentrations and no NH_4NO_3 was formed" to "when no NH_4NO_3 was formed and H_2SO_4 had a negligible contribution to the growth of >10 nm particles."
Page3057,line20	**Line435**:change "SOA likely contributed to" to "SOA possibly contributed to"
Page3058,line5	**Line441**: add "41121004, 41149901" after "(41176099, 21190050"
Reference	Add 9 references in **line 453-455, 470-472, 486-495, 503-507, 531-533, 566-568, 585-587, 590-592**.
Figures captions	change "N_{30nm}" to "$N_{<30nm}$",change "$D_{pg,i}$" to "$D_{pg,1}$" in **line 617-618,621, 624, 627, 630, 640-641, 645, 649, 653, 657.**