Response to the reviewer's comments on the manuscript "New particle formation in the fresh **fl**ue gas plume increase the effective particle number emissions of a coal-**fi**red power plant by Mylläri et al.

May 5, 2016

Dear editor and reviewers,

we thank the reviewers for comments and constructive suggestions. According to these comments, including short comments given by Stevens et al. and Junkermann, we have prepared the response to the comments and revised the manuscript. A response to the reviewers' comments is presented below, including the original comments written in italics.

Sincerely,

Mylläri and co-authors

Response to comments from Reviewer #1

Original comments are presented below in italics.

The results of this work are interesting but major revisions are needed before the manuscript can be published in ACP. The performed measurements and model calculations are not explained adequately but some relevant information is missing. The authors should also make sure that they are correctly citing and interpreting the previous work published on the topic (see the short comment by R. Stevens), and they should discuss uncertainties related to their measurements (see the short comment by W. Junkermann). The language of the manuscript should also be checked. More specific comments are presented below.

We modified the manuscript according to these comments. We added more information regarding experiments and modelling. For these, please see the responses for detailed comments below.

In addition, we took into account the comments from Stevens et al. and Junkermann and made the following changes to the manuscript (underlining indicates new text):

"Stevens et al.(2012) and Lonsdale et al. (2012) have compared these measurements to modelling results, which were based on emission inventory values. Modelling results indicated that secondary particle formation occurs in the plumes *after emission* from the stack and *the measurement results show correlation with the model especially at distances of 10-20 km*. Brock et al. (2002) argue the secondary particle formation to begin at 2 hour aged plume."

"In this study the power plant plume diluted to background levels in 2 km (200-400 seconds) which is faster than in other in-flight measurements (Stevens et al., 2012; Junkermann et al., 2011). This difference may be because *the dilution of plume and other processes are affected by source strength, background concentrations, and meteorology (*Stevens et al., 2012*).* In our study, we collected high-time-resolution data close to the power plant stack, which enable us to model the plume dilution on a detailed scale. From this, we were able to observe that while SO_2 and CO_2 were already diluted to

background levels at a distance of 2 km – in agreement with the dilution modeling - the effect of the source to the aerosol number concentration was distinguished at distances >2 km. We attribute this to nucleation taking place in the ageing plume"

"According to modelling results of Stevens et al. (2012), atmospheric new particle formation via coal combustion originated sulphuric acid nucleation begins at *1 km* distance from the source whereas the sulphuric acid formation begins right after emission. Our study therefore *supports this previous modelling work by showing that* nucleation may take place in the aged plume and being the most effective after 400 seconds, corresponding approximately 2 km distance from the emission source in atmosphere."

Regarding comments from Junkermann, the diffusion losses of particles were included to the supplementary information and discussed in the main text:

"The data was recorded based on gps-coordinates which were used to calculate distances from the stack, and the distances were changed to correspond plume age using wind speeds 6.5 m s^{-1} and 4.0 m s^{-1} (LIDAR, S3)." Diffusion losses for the particles in the sampling lines were calculated based on the measurement setup. The calculation showed that nearly 70 % of the 2.5 nm particles in diameter was lost in the sampling lines and thus the total concentration shown in Figure 3 can be higher than shown here. The vertical lines denote the 2 km distance from the stack. Figure 3 shows the dilution time scale of the flue gas in terms of CO_2 and SO_2 in both operation conditions. Same trend in SO_2 and N_{tot} concentrations as observed in Table 1, was measured by instruments installed in the helicopter; in ``FGD+FF off'' situation the particle and $SO_2$ concentrations were higher than the ``FGD+FF on'' situation. It should be kept in mind that in ``FGD+FF off'' situation only one of the two flue gas cleaning systems was bypassed."

In addition, flight direction and wind direction data during the measurements were compared. Those can be seen now in Figure 1. The right wind directions were corrected to the manuscript. The date of the measurement and flight time information were included in the manuscript.

Page 1, line 14: Can it really be concluded based on this study that "flue gas nucleation is more efficient than natural atmospheric nucleation"?

We modified the sentence to "In addition, results indicate that flue gas nucleation is more efficient than predicted by using atmospheric aerosol modelling."

Page 2, line 21–23: This statement is too general. For example, SO2 does not affects the climate directly but because it forms sulfuric acid, which affects particle formation.

We modified the sentence according to comment. It is now "In addition to CO_2 emissions, known to have climatic effects, coal combustion causes emissions of other harmful pollutants like NO_x, SO_2, and particulate matter, all decreasing the air quality and increasing health related risks but also affecting climate directly and indirectly. For instance, SO_2 affect the climate indirectly because it tends to oxidize in atmosphere and form H_2SO_4, which affects particle formation."

Page 3, line 66–76: The aims of the study should be expressed more clearly in the end of the introduction.

Similar comment was given also by Reviewer #3. We modified the end of the introduction so that it describes better the aims of the study: "The aim of this study was to characterize how the atmospheric emissions from a 726 MW coal-fired power plant depend on flue gas cleaning, i.e. desulphurization plant and fabric filters (later referred as "FGD+FF off" and "FGD+FF on"). In addition to the stack measurements for pollutants, the study aimed to show how the flue gas cleaning affects real atmospheric concentrations of emitted CO_2, SO_2 and particles. The study included experiments conducted in the stack of the power plant, measurements conducted with a helicopter equipped with instruments for CO_2, SO_2 and particles, and flue gas plume dispersion and aerosol process modelling. "

Following text was removed from the end of the introduction because its information is included in the experimental section: "The power plant has two boilers with separate flue gas cleaning systems. The measurement equipment was installed into two locations; into a helicopter, which enabled the measurement of real flue gas plume in the atmosphere, for the first time, and into the stack. The measurements in the flue gas plume and in the stack were conducted for two different flue gas cleaning situations, i.e. when the flue gas desulphurization unit including fabric filters was in operation (later called as ``FGD+FF on'') and when it was bypassed (later called as ``FGD+FF off'')."

Page 3–4, Sect. 2: The section describing the measurements is missing some relevant information. First of all, it is not told how long the measurement period was (if the measurements were conducted during only one day or several days etc.) In addition, many instruments are mentioned (page 4, line 106–109) without explaining what they measure or what their working principle is. Also, when the weather conditions during the study are described (page 4, line 97–103) it is not explained if the given values for different variables are means for the measurement period or something else.

Unfortunately the original text did not describe the lengths of measurement periods. This information has been written now more clearly in the manuscript. Descriptions of instruments used in the study were modified. Now those include also citations for appropriate publications to guide reader to find more information if needed (LIDAR: Pearson et al., 2009; FPS: Mikkanen et al., 2001; CPC: Agarwal et al., 1980; SMPS: Wang and Flagan 1990; ELPI: Keskinen et al. 1992; EEPS: Mirme 1994). The weather conditions are now given by ranges (min-max) in main text and in one table presented in the supplementary material. Also this is now mentioned in the manuscript.

Page 6, Sect 2.1.1: The section describing how particle formation rates were calculated is unclear. The authors should explain more clearly what they did, and define what they mean with nucleation/formation rates (especially, it is important to know at which size they are determined). Showing the equations used for calculating the formation rates and growth rates would help at understanding the calculations better. If I understand correctly, the authors first calculate Jnuc (at some size smaller than 2.5 nm) by assuming that it depends on sulfuric acid concentration, and then estimate the particle formation rate at 2.5 nm by utilizing a revised version of the so-called Kerminen-Kulmala equation. It is unclear how realistic these calculations are with all the assumptions. Furthermore, it remains unclear if the authors determined particle formation rates only from the parametrization, or also using the measured particle size distributions, which would be very useful (see also the comment related to this on the next page).

The model description has now been clarified in the revised version of the manuscript. Moreover, the assumptions behind the model are discussed extensively in the last paragraph of Section 3.4.

Page 7, line 200: The correct terms are "electrical mobility equivalent diameter" and "aerodynamic equivalent diameter". In addition, it should be specified that the mean diameters are geometric means (as they probably are).

The correct terms were changed to the manuscript and it was specified that they actually are geometric means.

Page 7, line 206: It should be explained more clearly why the difference in the mean diameters indicates that the density is higher than 1 g cm-3.

"Figure 2 shows the particle number size distributions of flue gas in the stack in both cleaning conditions. These were measured using an electrical low pressure impactor (ELPI) and a scanning mobility particle sizer (SMPS) in both ``FGD+FF on/off'' cases. In the ``FGD+FF on'' case the SMPS measurement is a median value over few hours of operation due to low particle number concentrations in the stack. Based on the SMPS measurement the particle geometric mean electrical mobility equivalent diameter was 80 nm and the width of particle number size distribution (geometric standard deviation, GSD) was 1.45 for ``FGD+FF off'' case. In comparison, the geometric mean electrical mobility equivalent diameter was 31 nm for ``FGD+FF on'' and the width of particle number size distribution was 2.15. Based on the measurements using the ELPI geometric mean aerodynamic equivalent diameter was 141 nm and GSD was 1.41. The difference in mean diameters measured using the ELPI and the SMPS comes from the differences in size classification principles of these instruments and enables the determination of effective density of measured particles. The effective density measurement and calculation is based on the relation between the electrical mobility equivalent diameter and the aerodynamic equivalent diameter of the particle (see Ristimäki et al. 2002). In this study case the difference in equivalent diameters indicates effective density larger than unit density for emitted particles (approximately 3.1 g cm^{-3}). In comparison, Saarnio et al. (2014) used effective density of 2.5 g cm^{-3} to convert the electrical mobility diameter measured using SMPS to aerodynamic diameter. *When studying ``FGD+FF on'' case the particle concentrations were so low and thus accurate determination of mean particle size was not possible from the particle size distribution measured by the ELPI.*"

New citation related to the calculation of effective density of particles was included into the manuscript:

Ristimäki et al., 2002 On-line measurement of size distribution and effective density of submicron aerosol particles; Journal of Aerosol Science, vol 33, num 11, pp. 1541-1557.

Page 8, line 209–211: Can it be concluded that the mean aerodynamic diameter and the mean mobility diameter are similar in this case, when there seem to be so few data points from ELPI based on Fig. 2?

This was again very valuable comment. It is true that in "FGD+FF on" case the effective density cannot be determined accurately. The sentence was modified.

Page 9, line 240–242: It is not clear for me where these "closest background values" were obtained and why they were subtracted from the measurements.

The closest background values referred the upwind side (from the stack) measurements between headwind and downwind approaches. We modified the sentence to consider only the mean background

concentration during the flight loops at the upwind side of the stack: “Respectively, the N_{tot} reached nearly to background concentrations after 200 seconds and 300 seconds. The background gaseous concentrations for each measured gaseous component were 403 ppm and 2-8 ppb, for CO_2 and SO_2 respectively. The boundary layer mixing started during the ``FGD+FF on'' measurements and thus the background values measured from the upwind side flight loops from the stack were averaged and subtracted from both ``FGD+FF on/off cases''.”

Page 9, line 249: Can it be concluded that particle concentration reached this high value as the concentration seems to fluctuate very strongly based on Fig. 3?

It is true that the data fluctuated significantly. We modified the text which is now “Based on Figure 3a, for ``FGD+FF off'' case the background particle concentration was 1430 cm-3, after 200 seconds the concentration was at the background level and after 400 seconds it increased significantly, even up to average level of 5 000 cm-3.”

Page 9, line 255: These increases cannot be seen in Fig. 3.

Descriptions regarding to increases were removed from the text.

Page 11, line 266. How these nucleation rates were calculated? If they were calculated using measured particle concentration, authors should explain the method they used. Also, these values should then be compared to the modelled values. It would also be useful to show the time series of nucleation rates; large ranges are now given which do not really tell how high nucleation rate was most of the time.

These formation rates were calculated from mean slope of increasing concentrations.

Page 12, line 278: It is too vague to state that “after that more small particles (and some larger particles are detected”. The authors should specify which particle sizes they mean, and how much more these were observed.

That is true. Taken the measurement uncertainties regarding the measurements by the EEPS into account, we modified the paragraph. It is now “The particle size distribution measurement made by using the EEPS (SI5) supports the results for total particle number measurement made by the CPC (Figure 3), i.e. in terms of particles the flue gas is diluting in 0-300 seconds in ``FGD+FF off''. In addition, the particle size distributions measured by the EEPS indicates slight increase of nanoparticle concentrations during the dilution and dispersion of the flue gas in the atmosphere”.

Page 12, line 301–303: The values of error and R^2 for different cases should be shown for example in a table.

The values for MREs and R^2 are now shown in table form.

Page 12, line 305–306: It would be good to show a figure about SO2 concentration.

Figure about the SO_2 concentrations was added to the supplementary information.

Page 14, line 319–320: The atmospheric concentration of sulfuric acid can vary a lot depending on the environment. Therefore, it would be good if the authors referred here also to some articles reporting sulfuric acid concentration at a site similar to this study.

We included two citations for studies reporting atmospheric sulfuric acid concentrations: Mikkonen et al., (2011, ACP), which report that H_2SO_4 concentrations varied between $1.86 \cdot 10^5$ -$2.94 \cdot 10^6$ molec cm^{-3}, and Sarnela et al., (2015, AE) which reported the sulfuric acid concentrations of 0.38-0.75 ppbv for Finnish industrial and non-industrial area.

Page 14, line 322: Based on Fig. 6, OH concentration seem to be practically zero in the beginning of the simulation. Is that true?

That is not true, for some reason the y-axis was limited from 1e2 onwards. The y-axis scale has now been changed.

Page 15, line 332: To which time periods the mean values presented here correspond? Reporting the mean values of nucleation rate for the whole measurement period is not reasonable.

The mean values are calculated over the whole measurement periods.

Page 15, line 330–340: As mentioned above, the nucleation rate calculations are not explained clearly and therefore it is difficult to follow when the authors mention different nucleation/formation rates. For example, it is not clear for me, if "apparent particle formation rates" calculated from CPC data are presented somewhere in the manuscript. It is also not explained how growth rates were determined. In addition, the authors should refer to some article more relevant for this study than Kulmala et al. (2001) when discussing previous observations on growth and formation rates.

The phrase "apparent particle formation rates" was removed and changed to "Furthermore, in our measurements the particles were detected at the lowest CPC detection limit which was 2.5 nm, $J_{2.5}$." In addition more relevant article was added Stoltzenburg et al., 2005.

Page 15, line 353–354: What if too low values of nucleation rates are due to the incorrect assumptions of the model? The authors should add some discussion about the uncertainties related to different assumptions in their calculations.

The uncertainties in the model calculations are discussed in the last paragraph of Section 3.4.

Page 15, line 357–358: It would be good if authors referred here to the observations of OH concentration made in some environment similar to the site of this study,

Two citations were included: Berresheim et al., (2002 JGR) which reports median value for OH concentration was $0.25 \cdot 10^6$ molec cm^{-3} in Mace Head, and Kuang et al. (2008 JGR) which reports OH concentrations of 10^6-$2 \cdot 10^7$ molec cm^{-3} in Atlanta.

Page 15, line 360: Why NOx concentrations are not shown?

We used in the Gaussian model the NO_x concentrations from the stack measurements. In principle, we think that it wouldn't bring major benefits to show the time series NO_x because it is practically similar than for time series for CO_2.

Page 16, Table 2: It should be stated clearly in the table caption that the results shown there are from a parametrization. In addition, it is not clear for me what is meant by "(1 cm-3 (600 s)-1)".

The caption was modified. The values in the table were recalculated to $cm^{-3}s^{-1}$

Page 16, line 366: The authors could refer here also to some articles discussing the role of other compounds besides sulfuric acid in atmospheric particle formation.

We refer now on Ehn et al. (2012) related to role of ELVOCs in atmospheric particle formation, and on the study of Arnold et al. (2012), which reports sulphuric acid concentrations for combustion engine engine exhaust but also indications on organosulfates in particle formation:

Ehn, M., Kleist, E., Junninen, H., Petäjä, T., Lönn, G., Schobesberger, S., Dal Maso, M., Trimborn, A., Kulmala, M., Worsnop, D.R., Wahner, A., Wildt, J., Mentel, T.F. Gas phase formation of extremely oxidized pinene reaction products in chamber and ambient air (2012) Atmospheric Chemistry and Physics, 12 (11), pp. 5113-5127.

Arnold, F., Pirjola, L., Rönkkö, T., Reichl, U., Schlager, H., Lähde, T., Heikkilä, J., Keskinen, J. First online measurements of sulfuric acid gas in modern heavy-duty diesel engine exhaust: Implications for nanoparticle formation (2012) Environmental Science and Technology, 46 (20), pp. 11227-11234.

Page 17–18, line 408–460: The conclusions of the study about the climate effects of the emissions of a coal-fired power plant should be stated here in a more concise and clear way. Now the conclusions remain rather vague.

The aim of the conclusions and discussions regarding climatic effects was to link the results with larger topics. Based on this comment and nearly similar comment from Reviever #3, we decided to remove the last paragraphs of Discussion and Conclusions sections. In addition, we modified the conclusion also based on short comments from Stevens at al. and Junkermann et al.

Page 1, line l4: This sentence should be rephrased.

We modified the sentence to ”In addition, results indicate that flue gas nucleation is more efficient than predicted by using atmospheric aerosol modelling.”

Page 5, Fig. 1: It should be explained in the figure caption what different colors (blue and black) mean.

The caption was rephrased: “Helicopter flight routes. The wind blew in the angle of 216°±5.51° (based on LIDAR data) and the flight direction was 213°±4.14° (based on GPS data for helicopter) in ``FGD+FF off'' (blue circles). Corresponding angles for ``FGD+FF on'' case (black circles) were 220°±6.25° (wind direction based on LIDAR data) and 223°±5.66° (flight direction based GPS data for helicopter). The triangular shapes (black and blue lines) show the helicopter GPS coordinates that have been taken into account in the calculations.”

Page 7, line 172: The equations should be numbered and shown on their own lines (also elsewhere in the manuscript).

These changes have been made like proposed.

Page 9, line 223: This sentence should be rephrased.

The sentence was changes to: “Figure 3 shows the measured flue gas plume concentrations as a function of plume age.”

Page 10, Figure 3: The figure is unclear. It is difficult to see different line as they are on top of each other. It might also be a good idea to present at least particle concentration data using a logarithmic scale. On the line 247 authors refer to Fig. 3a, but there are no “a” and “b” marked in the figure. It would also be good to mention in the figure caption or in the text which instrument was used for measuring Ntot shown in the figure.

The figure has been improved so that data series can be better compared with each other. The scaling of the axis is still linear (no concentration differences of several magnitudes) but the N_{tot} curve is in a different position compared to CO_2 and SO_2. Labels a) and b) were added and the measurement method for N_{tot} was added to the caption.

Page 11, Figure 4: The color bar is missing the label.

The color bar label was added.

Page 12, line 272: “changing in same ages” should be rephrased.

The sentence was removed.

Page 12, line 274–276: The sentence starting with “Figure 4...” is unclear.

The sentence was removed.

Page 12, Fig. 5: This figure is unclear due to errorbars, and it is difficult to separate red lines from each other. In addition, it is not explained in the figure caption which lines represent which stability classes.

The Figure 5 was modified according to the comment: errorbars were removed and legend was modified to show stability classes.

Page 16, line 370: “this studied power plant” should be rephrased.

The sentence was modified to “Each power plant (over 50 MW) in EU has emission limits for SO_2, NO_2, and particle mass concentrations, for the studied power plant the limits are 600 mg Nm^{-3} (210 ppm), 600 mg Nm^{-3} (290 ppm), and 50 mg Nm^{-3}, respectively.”

Page 16, line 371: “Table 1 results with” should be rephrased.

The sentence was modified to “Comparison of the results in Table 1 with these emission limits shows that the emissions were clearly below these limits when the power plant operation was normal (``FGD+FF on'').”

Page 16, line 375: It is not clear for me what is meant by “the amount of H2SO4 of new aerosol particles”

The sentence was modified to “In addition to primary emissions, flue gas cleaning systems seemingly affect also the compounds which can act as precursors for new particles; e. g. SO_2 tends to oxidize in the atmosphere to SO_3 and, further, to form H_2SO_4 which can nucleate or condensate to particle phase.”

Page 17, line 399–400: This sentence is unclear and it should be rephrased.

The sentence was modified to "For instance, rough estimates for particle number emission factors can be calculated by comparing the measured particle number concentration with the simultaneously measured CO2 concentration of the flue gas plume (see e.g. Saari et al. 2016). By utilizing this method, for particles existing in the flue gas plume in ages of 25–55 seconds the emission factor in respect of CO_2 was $2.0 \cdot 10^{10}$ $(g\ CO_2)^{-1}$ and in ages over 400 seconds $8 \cdot 10^{10}$ $(g\ CO_2)^{-1}$ in the "FGD+FF off" case. Similarly, in the "FGD+FF on" case the emission factors were $4 \cdot 10^{9}$ $(g\ CO_2)^{-1}$ (for aerosol dispersed 55-85 seconds in the atmosphere) and $3.74 \cdot 10^{10}$ $(g\ CO_2)^{-1}$ (for aerosol dispersed more than 500 seconds in the atmosphere). "

One reference was added: Saari, S., Karjalainen, P., Ntziachristos, L., Pirjola, L., Matilainen, P., Keskinen, J., Rönkkö, T. (2016) Exhaust particle and NOx emission performance of an SCR heavy duty truck operating in real-world conditions. Atmospheric Environment, 126, pp. 136-144, 10.1016/j.atmosenv.2015.11.047.

Response to comments from Reviewer #3

Overall, the major problem I see with this paper is lack of discussion on uncertainties related to their measurements (see detailed short comment by W. Junkermann). I urge authors to compare and contrast the results of their work and those presented in Junkermann et al. (2011, 2015) and others.

We have taken into account the comments from W. Junkermann in our revised manuscript. This includes adding the date of the measurement, wind direction from LIDAR, helicopter flight directions and sampling losses for particles in helicopter measurements into the manuscript. In addition, we checked that the manuscript text includes relevant information on the question related to semi-volatile particles in stack measurements.

Comparison of the results of our study with the results reported by Junkermann et al. cannot be made very straightforward because their study is actually very different when compared with our study. This is e.g. due to the lack of information shared regarding emission reduction systems used in their study, different time scales studied and different particle size ranges covered. However, we see that our study and studies reported by Junkermann et al. fulfills quite efficiently each other. Junkermann et al. (2015) studied "Size distributions measured within the centre of the first (12 km) and last (130 km) plume crossing" while our study focused on particles very near the source. Thus we made comparisons at very general level; e.g. Junkermann et al. (2011) reports that "our results show that flue cleaning technology actually introduces a new problem, in the form of increased emissions of ultrafine particles". Role of ultrafine particles is topic also in our study. In addition, Junkermann et al 2015 reports that the particle size increases as a function of plume ageing in the atmosphere. This has connection with our study, where new particle formation was measured in the flue gas plume.

Page 1, Line 9-10: What makes you think that these are actually newly formed particles in the flue gas plume when you are not measuring sub-3nm particles? New particles are those closer to 1 or 1.5 nm in

diameter, smaller than most instruments can measure (e.g. PSM can measure particles of 1 nm diameter which was not operated in this study). Please justify this?

Good comment. We modified the abstract according to this comment. “However, the atmospheric measurements indicated that new particles larger than 2.5 nm are formed in the flue gas plume, even in the very early phases of atmospheric ageing.” Unfortunately we did not have the PSM in our measurement setup.

Page 1, Line 13: There is no sufficient evidence to conclude "flue gas nucleation is more efficient than natural atmospheric nucleation" and also, it contradict to what authors discuss on page 14, line 333-336.

This similar comment was also given by Reviewer #1. We modified the sentence.

Page 3, Line 67-74: "The power plant has two boilers with separate ----------bypassed (later called as “FGD+FF off”). This all should moved to Experimental section, and instead discuss here measurements planned and major goals of this study.

This similar comment was also given by Reviewer #1. We moved the sentences to experimental section and modified the end of the introduction more to discuss the aims of this study.

Page 4, Line 96: What do you mean by weather conditions were quite stable? I would like to see time series or table for detailed weather conditions during the measurement time period, if available at all? You can include it in supplementary material.

We meant by stable weather conditions that variations in wind direction and wind speed, temperature, radiation and visibility were small. Those variations were included in the text already in the original manuscript; however, we added an additional table to the supplementary. Finally, we removed “quite” from the sentence.

Table 1/2: In both the tables, I would like to see nucleation mode particles in the particle size range of 2.5 nm to 15 nm diameter alongside total number concentration (as shown by Ntot). I believe you report Ntot from CPC measurements and SMPS calculated Ntot will give Ntot>15nm so CPC Ntot minus SMPS Ntot would probably give you rough estimate of nucleation mode particles.

Unfortunately, our measurement data does not allow this kind of analysis. Our measurement setup in the stack was designed so that we could study the non-volatile particles in the flue gas. Thus we do not have data from stack measurements related to nucleation mode particles.

Fig. 3: This figure needs to be improved significantly. The font size for all axes is too small. Why delta Ntot shown? It makes more sense to show Ntot. It is difficult to differentiate the background lines for SO2 and CO2, simply remove it and state the background values in the figure caption, that should be enough. Include labels "a" and "b" as you used in the text. Also include nucleation mode particles (2.5-15 nm diameter range) as a function of plume age as suggested above.

Thank you for your very good comment. This was pointed out also by Reviewer #1. We have modified the figure like you and Reviewer #1 proposed. ΔN_{tot} is shown the net effect of the particle formation. Regarding to nucleation mode particles (proposed particle size range 2.5-15 nm diameter range), please see our response on previous comments. In addition, the calculation based on CPC and EEPS data increases significantly uncertainties thus decreases the quality of data so much that we would not like to present it this paper.

Page 11, Line 265-279: Authors state that "EEPS particle size distribution data is noisy, can show maximum of 67% wrong compared to SMPS, and also can not be compared with CPC data" If that is so then Fig. 4 should be removed or at least moved to supplementary for readers and discuss in the main text very briefly.

The figure was moved to Supplementary Information.

Page 14, Line 330-331: " According to the scheme applied here", be specific and give details of scheme applied here or in the methods section.

One equation was added to the manuscript from Lehtinen et al. (2007). The sentence was modified " According to the scheme applied here (see equations 4 and 5)…"

Page 16, Line 386: I do not agree with authors stating that " but this study shows that nucleation can take place in lower SO2 concentrations." From Table 1 and figure 3, the SO2 concentrations were much higher than a ppb level and with 10^5-10^6 cm^-3 OH concentrations and lower CS, it should form sufficient H2SO4 for particle nucleation to occur.

Good comment. The part has been modified based on the short comment by Stevens et al. and the sentence was removed. The nucleation indeed does take place (see Fig.5 in the revised manuscript). However, according to the model calculations, practically all of the nucleated particles (having an initial size of 1.5 nm), did not reach detectable sizes due to coagulational scavenging.

Page 1 : Suggest revising the title to "New particle formation in the fresh flue gas plume from a coal-fired power plant in Helsinki increases the effective particle number concentrations".

We think that the location of the power plant is not important; however the emphasis of the title should be in the flue gas cleaning technologies which are, in our opinion, far more important in terms of the emissions. Based on this we modified the title: "New particle formation in the fresh flue gas plume from a coal-fired power plant: effect of *flue gas cleaning"*

Page 1, Line 5: Replace "nucleation particle precursor formation" with "particle formation precursors"

Replacement was made.

Page 2, Line 23: replace "particles" by "particulate matter".

Replacement was made.

Page 2, Line 25-27: " However, with proper combustion and flue gas cleaning ---------- than CO2 can be decreased", support this statement by reference

The references were added (Helble, 2000; Saarnio et al., 2014), they were missing from the text but were present at the references list.

Page 3, Line 100-101: " The background aerosol concentrations for ---------- were: CO2 403 ppm, SO2 less than 2-8 ppb." Do you mean to say the background gaseous concentrations were?

The sentence was corrected to consider "the background gaseous concentrations".

Page 4, Line 107: correct as "TSI Inc."

This was corrected.

Page 4, Line 115-116: Particle size distribution was measured in what size range?

Particle size range was added "… from 5.6 nm to 560 nm".

Page 10, Line 236: I believe, the atmospheric background SO2 concentration is much lower than 25 ppb.

Good comment. We checked the background SO_2 concentration and corrected the value into the manuscript to be "2-8 ppb". These values are from helicopter flight upwind the stack.

Fig.5: replace " (above) and 'c' and 'd' (below)," by " (top panel) and 'c' and 'd' (bottom panel)," if that is what you meant to say.

Corrections were made as suggested.

Page 7, Line 182: Authors state that "background concentration of NOx is practically zero". It should be justified.

The sentence was changed to "To support this, the study of Pirjola et al. (2014) indicates that in the harbour area close to the power plant studied here the NO_x concentration level is typically clearly lower than 100 ppb."

Page 13, Line 323: I think, the atmospheric background value of CS is slightly lower than you report, usually of the order or 10^-3 s^-1.

This value was calculated based on the SMEAR III station data and it is at the ground level, thus the CS given in our manuscript might be an overestimation of the real CS at the stack height in the atmosphere.

Fig. 6: figure caption needs to be improved e.g. time development of [H2SO4] (blue line), ...The OH concentration seems to be zero or lower than 10^2 initially, please re-scale y-axis

We agree. Y-scale of the figure was changed.

J25 refers to particle formation rate at particle size of 2.5 nm, right? if so then replace J25 to $J_{2.5}$.

It was replaced.

Page 15, Line 352: it should read as - they are "relatively" low. It is very difficult to compare these values with literature values as you do not mention the time of measurement (see specific comment)

Information about time of flights and the date were added to the manuscript. “The measurements were made 24.3.2014 in two separate one hour periods (see specific times from S2, the black rectangulars; the first illustrates “FGD+FF on” case and the latter “FGD+FF off” case). “

Page 16, Line 407: "Based on that knowledge, it can be assumed that the formed particles are more scattering than absorbing." can we really conclude this based on results presented here?

We significantly modified the discussion and conclusion sections regarding to this comment (removed most of text). Nearly similar comment was given also by Reviewer #1. The aim of these texts was to bring larger perspective into the paper.

Page 16: the last paragraph of 3.5 discussion section is not in light of results presented in this work. e.g. in countries like China and India, there are other major sources e.g. transportation which contribute significantly to degraded air quality (total particulate matter). I would suggest to remove this paragraph completely and discuss your results in light of previous studies on particle formation in power plant plume rather than generalizing way beyond the scope of this study.

The paragraph was removed.

Page 18: The last paragraph of conclusion section mostly like introducing the topic, instead it should state what are the implications of this study.

The paragraph was removed.

Finally, list of new references included in the manuscript:

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New particle formation in the fresh flue gas plume ~~increase the effective particle number emissions of~~ from a coal-fired power plant: effect of flue gas cleaning

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Abstract. Atmospheric emissions, including particle number and size distribution, of a 726 MW_{th} coal-fired power plant were studied experimentally from power plant stack and from flue gas plume dispersing in the atmosphere. Experiments were conducted under two different flue gas cleaning conditions. The results were utilised in a plume dispersion and dilution modelling taking into account ~~nucleation particle~~ particle formation precursor (H_2SO_4 resulted from the oxidation of emitted SO_2) ~~formation~~ and assessment related to nucleation rates. The experiments showed that the primary emissions of particles and SO_2 were effectively reduced by flue gas desulphurization and fabric filters, especially the emissions of particles smaller than 200 nm in diameter. Primary pollutant concentrations reached background levels in 200–300 seconds. However, the atmospheric measurements indicated that new particles larger than 2.5 nm are formed in the flue gas plume, even in the very early phases of atmospheric ageing. The effective number emission of nucleated particles were several orders of magnitude higher than the primary particle emission. Modelling studies indicate that regardless of continuing dilution of the flue gas, nucleation precursor (H_2SO_4 from SO_2 oxidation) concentrations remain relatively constant. In addition, results indicate that flue gas nucleation is more efficient than ~~natural atmospheric nucleation~~predicted by using atmospheric aerosol modelling. Especially, the observation of the new particle formation with rather low flue gas SO_2 concentrations changes the current understanding on the air quality effects of coal-combustion. The results can be

used to evaluate the optimal ways to achieve better air quality particularly in polluted areas like India and China.

1 Introduction

In global scale, nearly 40 % of annual production of electricity is covered by coal combustion (EU, 2014). In addition to CO_2 emissions, known to have climatic effects, coal combustion causes emissions of other harmful pollutants like NO_x, SO_2, and ~~particles~~particulate matter, all decreasing the air quality and increasing health related risks but also affecting climate ~~.~~directly and indirectly. For instance, SO_2 affect the climate indirectly because it tends to oxidize in atmosphere and form H_2SO_4, which affects particle formation. Coal combustion related air quality problems exist especially in developing countries like China (Huang et al., 2014) where the power production is not always equipped with efficient flue gas cleaning systems. However, with proper combustion and flue gas cleaning technologies the fine particle emissions of coal combustion can be decreased to very low level and also the emissions of gaseous pollutants other than CO_2 can be decreased ~~.~~(Helble, 2000; Saarnio et al., 2014). Particle mass and number emission factors for the 300 MW coal-fired power plant with electrostatic precipitator (ESP) and flue gas desulphurization unit (FGD) have been reported by Frey et al. (2014): the emission for particle mass (PM1) was 0.18 ± 0.06 mg MJ^{-1} and for fine particle number $2.3{\cdot}10^9 \pm 4.0{\cdot}10^9$ MJ^{-1}. However, it can be expected that particle emissions and also the characteristics, such as particle size, are highly dependent on technologies used in the power production. Only few studies have reported particle number size distributions and mean particle diameter for the coal combustion emissions. The mean particle diameters have been reported to be between 100 nm (Frey et al., 2014; Yi et al., 2008) and 1 μm (Yi et al., 2008; Lee et al., 2013). According to Saarnio et al. (2014), chemical composition of particles in the efficiently cleaned flue gas after the FGD is shifted towards desulphurization chemicals. Interestingly, sulphate particle emissions from coal combustion with proper cleaning technologies can restrain the global warming due to cooling effect of the particles (Frey et al., 2014; Charlson et al., 1992; Lelieveld et al., 1992).

Due to the emission limits of power plants, driven by needs for healthier environment, emissions should be kept at minimum. This can be achieved by different technologies. Flue gas NO_x emissions can be reduced in the power plant boiler by applying low-NO_x burners, whereas SO_2 emissions can be reduced by flue gas desulphurization (FGD) (Srivastava et al., 2001). Particle emissions can be reduced by electrostatic precipitators (ESP) and fabric filters (FF). Very low emission levels can be achieved by these techniques. For example from particle emission point of view, ESP typically removes 99% (Helble, 2000) of the fine particles. Further, Saarnio et al. (2014) showed that desulphurization plant with fabric filters remove up to 97 % of the fine particles. Combination of these techniques would then remove 99.97 % of the fine particle emissions of the particles formed in combustion. However, particle emission as well as the effects of technologies can differ from these if

the emissions are measured from the diluted flue gas in the atmosphere. In principle, particle number and even particle mass can increase in the atmosphere for example due to the nucleation and condensation processes (Marris et al., 2012; Buonanno et al., 2012). However, there are very few observations of the processes in the diluting flue gas during the first few minutes after the stack.

Power plant plumes have been studied with aircrafts by measuring long distance cross-wind profiles of gases and particles (Stevens et al., 2012; Brock et al., 2002; Lonsdale et al., 2012; Junkermann et al., 2011). Stevens et al. (2012) and Lonsdale et al. (2012) have compared these measurements to modelling results, which were based on emission inventory values. Modelling results indicated that secondary particle formation occurs in the plumes after ~~10–20 km~~ emission from the stack ~~, whereas~~ and the measurement results show correlation with the model especially at distances of 10-20 km. Brock et al. (2002) argue the secondary particle formation to begin at 2 hour aged plume. Study of Brock et al. (2002) has focused on plume ages 0 to 13 hours old power plant plumes. However, Brock et al. (2002) do not report particle number concentrations for fresh flue gas. Cross-wind profiles shown in the study of Stevens et al. (2012) were from 5 km to a bit over 50 km distances, and these results were also used in Lonsdale et al. (2012). On the contrary, Junkermann et al. (2011) followed the plume centre line based on the SO_2 concentrations and made also few cross-wind profiles of the studied plume.

~~This study focuses on real atmospheric dilution and dispersion of CO_2, SO_2 and particles emitted~~ The aim of this study was to characterize how the atmospheric emissions from a 726 MW coal-fired power plant ~~. The power plant has two boilers with separate~~ depend on flue gas cleaning~~systems. The measurement equipment was installed into two locations; into a helicopter, which enabled the measurement of real flue gas plume in the atmosphere, for the first time, and into the stack. The measurements in the flue gas plume and in the stack were conducted for two different flue gas cleaning situations, ~~, i.e. when the flue gas desulphurization unit including fabric filters was in operation (later called~~ desulphurization plant and fabric filters (later referred as "FGD+FF ~~on")~~ ~~and when it was bypassed (later called as~~ off" and "FGD+FF ~~off~~on"). ~~The measurement of flue gas plume enabled studying the aerosol processes and flue gas dilution as a function of time and also in the vicinity of the source (from tens of meters to kilometers)~~In addition to the stack measurements for pollutants, the study aimed to show how the flue gas cleaning affects real atmospheric concentrations of emitted CO_2, SO_2 and particles. The study ~~comprises measurements made~~ included experiments conducted in the stack ~~and in the~~ of the power plant, measurements conducted with a helicopter equipped with instruments for CO_2, SO_2 and particles, and flue gas plume ~~with~~ dispersion and aerosol process modelling.

2 Experimental

The studied power plant is a base-load station located near Helsinki city centre, Finland. The power plant consists of two 363 MW_{th} coal-fired boilers. The energy is produced by coal combustion in 12 low-NO_x technology burners (Tampella/Babcock-Hitachi HTNR ~~low NO~~low-NO_x), situating at the front wall of the boiler. The properties of coal used in this study are listed in SI1. Combustion releases flue gases that are cleaned in electrostatic precipitator (ESP), semi-dry desulphurization plant (FGD), and fabric filters (FF) before the stack. There are separate flue gas ducts and flue gas cleaning systems for each boiler.

The flue gas was studied in two different locations: the flue gas plume, and a reference point inside the stack. Measurements were made at both locations with two different flue gas cleaning situations: "FGD+FF off" and with all cleaning systems ("FGD+FF on"). The measurement location in the stack was at the height of +35 meters above sea level. The flue gas temperature inside the duct was 78 $\pm$ 2 °C in normal operation conditions and 130 $\pm$ 13 °C during "FGD+FF off" situation. The flue gas plume concentrations were measured with a helicopter equipped with aerosol instruments. The flying altitude of the helicopter was 150 meters above ground level or higher which corresponds to the LIDAR (Halo Photonics Streamline Doppler lidar with full-hemispheric scanning capability, Pearson et al., 2009) (SI2) results for plume altitude. It should be noted that only the flue gases from the boiler under investigation were steered to bypass FGD and FF. Thus, in the "FGD+FF off" situation flue gas plume consisted of both the cleaned flue gas and the flue gas cleaned by ESP. This has to be kept in mind in the analysis of atmospheric measurements.

The measurements were made 24.3.2014 in two separate one hour periods (see specific times from SI2, the black rectangulars; the first illustrates "FGD+FF on" case and the latter "FGD+FF off" case). Weather conditions were ~~quite~~ stable during the study. The wind direction and speed were ~~210~~ 216°$\pm$ 5.51° (based on LIDAR data) and 6.5 m s^{-1} in "FGD+FF off" case and ~~260~~ 220°$\pm$6.25° and 4 m s^{-1} in "FGD+FF on" case, respectively. The marine boundary layer height was 246–258 meters and the planetary boundary layer heights were 360–530 meters. However the calculations were made within the marine boundary layer because the flue gas plume did not arise above it. The background aerosol concentrations for each measured gaseous component were: CO_2 403 ppm, SO_2 less than 2–8 ppb. The range of ambient temperature was 6.6–6.9 °C, the global radiation was ~~346–466~~ 347–466 W m^{-2} and the visibility was ~~over 30 000 meters~~ 29043–36293 meters (see standard deviations from SI2) .

The instrument installations in different locations are shown in SI3. The sampling of flue gas in the stack was performed with Fine Particle Sampler (FPS; Dekati Ltd., Mikkanen et al., 2001) with total dilution ratio (DR) of 27. Probe and dilution air temperatures were at 200°C. The sample was led to instruments: Condensation Particle Counter (CPC3776; TSI Inc., Agarwal et al., 1980), ELPI (Dekati Ltd., Keskinen et al., 1992), SMPS (Wang and Flagan, 1990) 0.6/6 slpm (DMA3071, CPC3775 ~~TS~~ TSI Inc.) and gas analysers for diluted CO_2 (model VA 3100, Horiba) and NO, NO_2 and NO_x (model

APNA 360, Horiba). Measurement data was also received from a normal operation monitoring of the emissions, including raw flue gas SO_2, NO_x, CO_2 concentrations and dust (SICK RM 230, calibrated based on SFS-EN 13284-1 standard). In contrast to stack sampling, the sample in the flue gas plume dilutes naturally and can be sampled to equipment without additional dilution of aerosol sample. The sampling inlet position in the helicopter is shown in ~~S3~~SI3. Natural dilution causes rapid changes in concentrations and, thus, high measurement frequency equipment were used in the helicopter. CPC3776 (TSI Inc.) was installed to measure the total particle number concentration, whereas Engine Exhaust Particle Sizer (EEPS, TSI Inc., Mirme,1994) was measuring the particle number size distribution at 1 Hz sampling frequency from 5.6 nm to 560 nm. Gas concentrations for CO_2/CH_4/H_2O (Cavity spring-down spectrometry Picarro model G1301-m CO_2/CH_4/H_2O Flight Analyzer) and SO_2 (Thermo Scientific Inc. model 43i SO_2 analyzer, with 5 second response time) were measured continuously with 1 Hz frequency.

Fig. 1 shows the helicopter measurement routes for "FGD+FF on" and "FGD+FF off" situations. The objective of flight routes was to follow the centre line of the flue gas plume. Helicopter flew both up and down of the plume; the gps-data was used to separate these two flight situations to calculate the distance and the age of the plume separately.

2.1 Model description: Gaussian plume model

The Gaussian plume model is a solution to an advection-diffusion equation that describes the changes in the pollutant concentrations due to advection of wind and turbulent mixing with the surrounding air (Stockie, 2011). Accordingly, the concentration of a pollutant i, C_i, emitted from a point-like source, can be expressed as follows:

$$C_i(x,y,z) = \frac{Q_i}{2\pi U \sigma_y \sigma_z} \exp(-\frac{y^2}{\sigma_y^2})[\exp(-\frac{(z-H)^2}{\sigma_z^2}) + \exp(-\frac{(z+H)^2}{\sigma_z^2}] \quad (1)$$

Here x, y and z are the spatial coordinates, aligned so that x axis corresponds to the wind direction, and H is the height at which i is emitted (stack height). Also, Q_i is the emission rate of i at the source, U is the mean wind speed, and σ_z as well as σ_y are the so called dispersion coefficients which reflect the spatial extent of the plume as a function of the downwind distance x. The dispersion coefficients were calculated using the parameterization of Klug (1969) and the atmospheric stability class, which is needed to calculate the dispersion coefficients. Atmospheric stability classes were estimated based on the measurements of the wind speed and solar radiative flux at the surface. Moreover, the pollutant concentrations were calculated along the centerline of the plume, the value of U was set to constant and equal to the average wind speed during the flights. Finally the value of z was set equal to the stack height (150 meters).

It is worth noting that the background concentration of ~~i~~ i is zero according to eq. 1: $C_i \to 0$ when $z \to \infty$ or $y \to \pm\infty$ However, the flue gas emitted from the stack was actually cleaner, in terms of particle number concentration, than the background air when the flue gas was cleaned properly. In

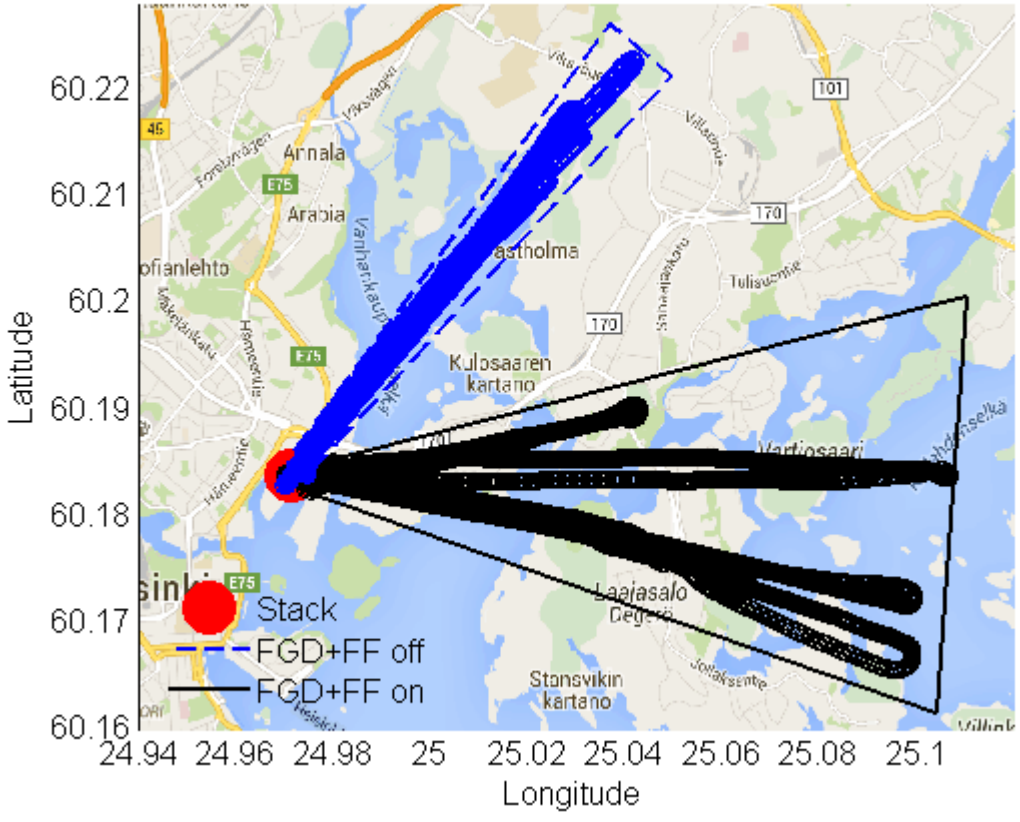

Figure 1. Helicopter flight routes. The wind blew ~~210°~~ in the angle of 216°± 5.51° (based on LIDAR data) and the flight direction was 213°±4.14° (based on GPS data for helicopter) in "FGD+FF off" ~~and 260 ° in~~ (blue circles). Corresponding angles for "FGD+FF on" case (black circles) were 220°±6.25° (wind direction based on LIDAR data) and 223°±5.66° (flight direction based on GPS data for helicopter). The triangular shapes (black and blue lines) show the helicopter GPS coordinates that have been taken into account in the calculations.

order to take into account for such cases, the following equation was used instead of eq. **??**:

$$\hat{C} = C_\infty + \frac{C_0 - C_\infty}{C_0} \cdot C_i \quad (2)$$

where C_∞ is the background concentration of i, and C_0 is its concentration at the source. It can be readily shown that eq. **??** is a solution the advection-diffusion equation underlying eq. **??**. Also, it is easily verified that $\hat{C} \to C_\infty$ when $z \to \infty$ or $y \to \pm\infty$. Finally, the value of Q_i in eq. **??** was chosen so that $\hat{C} \to C_0$ when $z \to H$ and x,$y \to 0$.

An important output of the model is the dilution ratio of the flue gas plume, DR, which is calculated ~~as follows DR(t)= (~~based on equation **??**.

$$DR(t) = \frac{[CO_2(t)] - [CO_{2,\infty}]}{[CO_{2,stack}] - [CO_{2,\infty}]} \quad (3)$$

In equation **??** [$CO_2(t)$] ~~- $CO_{2,\infty}$)/($CO_{2,stack}$- $CO_{2,\infty}$) where $CO_2(t)$~~and [$CO_{2,\infty}$] are the modelled CO_2 concentration at time t and the CO_2 concentration measured in the stack, respectively.

2.1.1 Model description: Nucleation rate and particle formation calculations

The particle appearance (driven by nucleation and growth) rates ~~at the lowest diameter detected by the CPC (~~for the particles 2.5 nm ~~)~~ in diameter were calculated using the parameterization developed by Lehtinen et al. (2007) ~~.~~ presented in eq. **??**. The key input parameters for the model are the nucleation rate (J_{nuc}), the particle growth rate (GR), and the coagulation sink which describes the rate at which clusters are removed via coagulational scavenging ($CoagS$). The parameter J_{nuc} is calculated based on the estimated sulphuric acid concentrations as function of plume age as detailed below, and the particle growth rates are calculated by assuming growth only via irreversible condensation of sulphuric acid. Also, $CoagS$ is calculated from the condensation sink CS (which is calculated in a fashion described below) using the eq. 8 in Lehtinen et al. (2007). Also, the initial size of the freshly nucleated clusters was varied, and the value of the shape factor (m in Eq. 6 in Lehtinen et al. (2007)) was set equal to –1.6.

$$J_x = J_{nuc} \cdot \exp(-\gamma \cdot d_1 \cdot \frac{CoagS(d_1)}{CS}) \quad (4)$$

The nucleation rates J_{nuc} in the studied plume were calculated using the parameterization developed by Kulmala et al. (2006) which has also been applied previously to model nucleation in plumes (Stevens et al., 2012, 2013). ~~Accordingly, J_{nuc} = A×$H_2SO_4$where A~~

$$J_{nuc} = A \times [H_2SO_4] \quad (5)$$

In equation **??** A=$1 \cdot 10^{-7}$ s^{-1} or A=$1 \cdot 10^{-6}$ s^{-1} and [H_2SO_4] (cm^{-3}) is the sulphuric acid concentration. The value of A=$1 \cdot 10^{-7}$ s^{-1} was chosen according to the study of Stevens et al. (2012, 2013). The initial size size of the nucleated particles was assumed to be of 1.5 nm

Formation of [H_2SO_4] was calculated assuming that it is produced only via the OH + SO_2 reaction and the only loss pathway for H_2SO_4 is condensation onto the particle surfaces. When steady-state is assumed, the ~~following equation is thus obtained~~ [H_2SO_4] ~~= $k_1 \times SO_2 \times OH/CS$ where k~~can be calculated from equation **??**.

$$[H_2SO_4] = k_1 \times \frac{[SO_2] \times [OH]}{CS} \quad (6)$$

In equation **??** k_1 is the reaction constant between OH and SO_2 (Table B.2 in Seinfeld and Pandis, 2008). The SO_2 concentrations were taken from the helicopter measurements, and the time development of CS and [OH] in the plume were modelled as follows. First, CS was calculated using the relation ~~CS= CS~~shown in equation **??**.

$$CS = \frac{CS_{stack}}{DR} + CS_{\infty} \times (1 - \frac{1}{DR}) \quad (7)$$

In equation **??** CS_{stack} ~~/DR + $CS_{\infty} \times$(1 − 1/DR) where CS_{stack}~~ is the condensation sink of aerosols measured in the stack, and CS_{∞} is the condensation sink of the background aerosols. The value of the latter parameter was calculated from the size distributions measured at the SMEAR III station (Junninen et al., 2009) which is located around two kilometers away from the power plant. Second, [OH] was calculated using the parameterization of Stevens et al. (2012) which has downward shortwave radiative flux at the surface and [NO_x] as main inputs. Value for the former parameter was taken from the measurements (using the value averaged over the measurement periods), and the NO_x concentrations were calculated ~~as follows:~~ from equation **??**.

$$[NO_x(t)] = \frac{[NO_{x,stack}]}{DR(t)} \quad (8)$$

In equation **??** [NO_{x}~~(t)= $NO_{x,stack}$~~] ~~/$DR(t)$ where $NO_{x,stack}$~~ is the NO_x concentration measured in the stack. It should be noted here that in the calculations the background concentration of NO_x is assumed to be of minor importance when compared to NO_x emitted by power plant. To support this, the study of Pirjola et al. (2014) indicates that in the harbour area close to the power plant studied here the NO_x concentration level is typically clearly lower than 100 ppb.

3 Results

3.1 Primary emissions of the coal-fired power plant

The SO_2 and particle emissions of the power plant were strongly dependent on flue gas cleaning system. This can be seen in Table 1 which shows flue gas concentrations for CO_2, SO_2, NO_x, O_2, particle number (N_{tot}), dust as well as flow rate in the duct in both flue gas cleaning conditions. In the shift from "FGD+FF off" to "FGD+FF on" situation the SO_2 concentration decreased nearly to

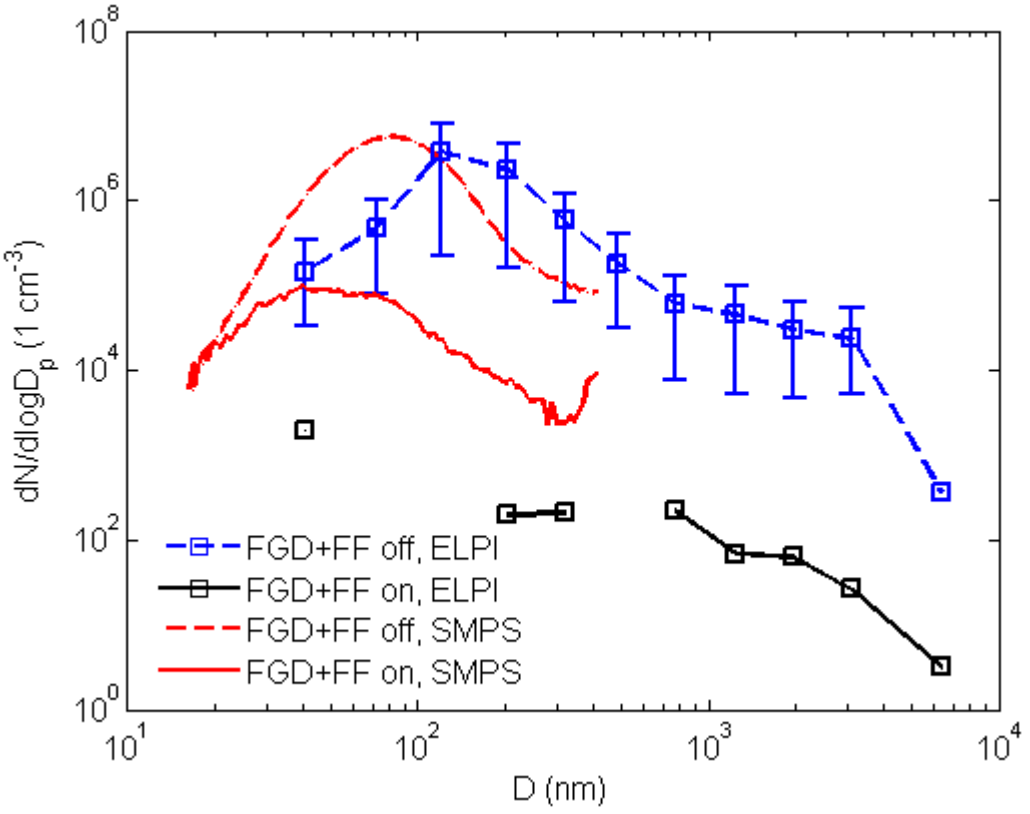

Figure 2. Particle size distributions measured with ELPI and SMPS from the flue gas in the stack. ELPI and SMPS data is shown in operation conditions, "FGD+FF on" and "FGD+FF off". The x-axis is aerodynamic diameter for ELPI data and electrical mobility diameter for SMPS data.

fifth part, the concentration of dust decreased by a factor of 50 and the N_{tot} decreased by a factor of four thousand. For other parameters the effect of FGD+FF was insignificant.

Figure 2 shows the particle number size distributions of flue gas in the stack in both cleaning conditions. These were measured using an electrical low pressure impactor (ELPI) and a scanning mobility particle sizer (SMPS) in both "FGD+FF on/off" cases. In the "FGD+FF on" case the SMPS measurement is a median value over few hours of operation due to low particle number concentrations in the stack. Based on the SMPS measurement the particle ~~mean mobility~~ geometric mean electrical mobility equivalent diameter was 80 nm and the width of particle number size distribution (geometric standard deviation, GSD) was 1.45 for "FGD+FF off" case. In comparison, the ~~mean mobility~~ geometric mean electrical mobility equivalent diameter was 31 nm for "FGD+FF on" and the width of particle number size distribution was 2.15. Based on the measurements using the ELPI ~~mean aerodynamic~~ geometric mean aerodynamic equivalent diameter was 141 nm and GSD was 1.41. The difference in mean diameters measured using the ELPI and the SMPS comes from the

Table 1. Flue gas concentrations of CO_2, SO_2, NO_x, O_2, total particle number (N_{tot}), dust, and flue gas flow rate in the stack. Mean values (+ standard deviation) are presented for both flue gas cleaning conditions ("FGD+FF on" and "FGD+FF off").

	FGD+FF off	FGD+FF on
CO_2 (%)	9.92 ± 2.2	10.3±0.96
SO_2 (ppm)	243±71.3	55.2±1.46
NO_x (ppm)	252±74	258±65
O_2 (%)	6.16±0.11	6.11±0.10
N_{tot} (cm^{-3})	$(1.8 \pm 0.2) \cdot 10^6$	420±640
Dust (mg/Nm^3)	188±82	4±1
Flow (Nm^3/h)	$(4.86 \pm 0.20) \cdot 10^5$	$(4.65 \pm 0.064) \cdot 10^5$

~~size classification principle of the ELPI, which is sensitive to particle density. In fact, the difference~~ differences in size classification principles of these instruments and enables the determination of effective density of measured particles. The effective density measurement and calculation is based on the relation between the electrical mobility equivalent diameter and the aerodynamic equivalent diameter of the particle (see Ristimäki et al. 2002). In this study case the difference in equivalent diameters indicates effective density larger than unit density for emitted particles (approximately 3.1 g cm^{-3}). In comparison, Saarnio et al. (2014) used effective density of 2.5 g cm^{-3} to convert the electrical mobility diameter measured using SMPS to aerodynamic diameter. When studying "FGD+FF on" case ~~there was no difference between aerodynamic particle diameter and mean mobility diameter and, thus no difference in the density of the particles.~~the particle concentrations were so low and thus accurate determination of mean particle size was not possible from the particle size distribution measured by the ELPI.

Flue gas sample from the stack was diluted with hot dilution air before the particle instruments and thus the particle number concentrations (Table 1) and particle size distributions (Figure 2) are for non-volatile particles. In combustion studies the hot dilution air is typically used to prevent the formation of liquid nucleation particles and to minimize the effects of condensation of semi-volatile compounds on particles. However, to ensure the measured particles were non-volatile and not affected by the dilution method itself, a thermodenuder (Rönkkö et al., 2011) was used periodically after the sampling and dilution. The thermodenuder did not affect the particle number size distribution, which confirms the non-volatile nature of the measured particles. Due to this non-volatility of the particles, the life time of the primarily emitted particles in the atmosphere can be longer than that of volatile particles, e.g. nucleation mode particles observed in vehicle exhaust (Lähde et al., 2009).

3.2 Atmospheric measurements

~~The measurement results are shown in~~ Figure 3 ~~describing the~~ shows the measured flue gas plume concentrations as a function of plume age. Diffusion losses for the particles in the sampling lines were calculated based on the measurement setup. The data was recorded based on gps-coordinates which were used to calculate distances from the stack, and the distances were changed to correspond plume age using wind speeds 6.5 m s^{-1} and 4.0 m s^{-1} (LIDAR, S3). The calculation showed that nearly 70% of the 2.5 nm particles in diameter was lost in the sampling lines and thus the total concentration shown in Figure 3 can be higher than shown here. The vertical lines denote the 2 km distance from the stack. Figure 3 shows the dilution time scale of the flue gas in terms of CO_2 and SO_2 in both operation conditions. Same trend in SO_2 and N_{tot} concentrations as observed in Table 1, was measured by instruments installed in the helicopter; in "FGD+FF off" situation the particle and SO_2 concentrations were higher than the "FGD+FF on" situation. It should be kept in mind that in "FGD+FF off" situation only one of the two flue gas cleaning systems was bypassed.

Plume dilution can be evaluated by the CO_2 concentrations (in Figure 3 a and b), which show that the "FGD+FF off" case dilutes to approximately background level in 200 seconds (0.74 km) and the "FGD+FF on" case in 300 seconds (1.5 km). The peak values for CO_2, SO_2 and N_{tot} were 3195 ppm, 2193 ppb, $3.\cdot10^4$ cm^{-3} in the "FGD+FF off" situation and 3254 ppm, 585 ppb, $0.4\cdot10^4$ cm^{-3}, respectively, for the "FGD+FF on". However, the dilution decreases the CO_2, SO_2 and N_{tot} concentrations in the atmosphere to 422 ppm, 52 ppb in "FGD+FF off" situation, and 473 ppm, 89 ppb in "FGD+FF on" situation. Respectively, the N_{tot} reached nearly ~~to~~ background concentrations after 200 seconds and 300 seconds. The background gaseous concentrations for each measured gaseous component were 403 ppm and ~~< 25~~ 2-8 ppb, for CO_2 and SO_2 respectively. The boundary layer mixing started during the "FGD+FF on" measurements and thus the ~~closest background values were~~ background values measured from the upwind side flight loops from the stack were averaged and subtracted from both "FGD+FF on/off cases". It can be noted that very near (first 10–50 seconds) the stack the helicopter was not in the plume. This can be seen from CO_2 and SO_2 concentration values presented in Figure 3a and 3b when approaching plume age zero. Thus, the dilution process is discussed below, mainly, from the maximum concentrations forward.

An increase in total particle concentration can be seen in Figure 3 after 400 seconds aged the flue gas plume. This tendency can be seen in both flue gas cleaning situations. Based on Figure 3a, for "FGD+FF off" case the background particle concentration was 1430 cm^{-3}, after 200 seconds the concentration was at the background level and after 400 seconds it increased ~~to 10~~ significantly, even up to average level of 5 000 cm^{-3}. Based on CO_2 measurements, the dilution of flue gas was practically complete at 200 seconds. Similarly, in "FGD+FF on" case after 500 seconds the particle concentration was slightly above background, after which increasing even up to 5 000 cm^{-3} after 700 seconds. Thus, the concentrations in the diluted and aged flue gas plume were higher than the background and significantly higher than could be expected based on the primary particle concentrations and observed dilution profiles. ~~There is a moderate increase in CO_2, and SO_2 concentrations~~

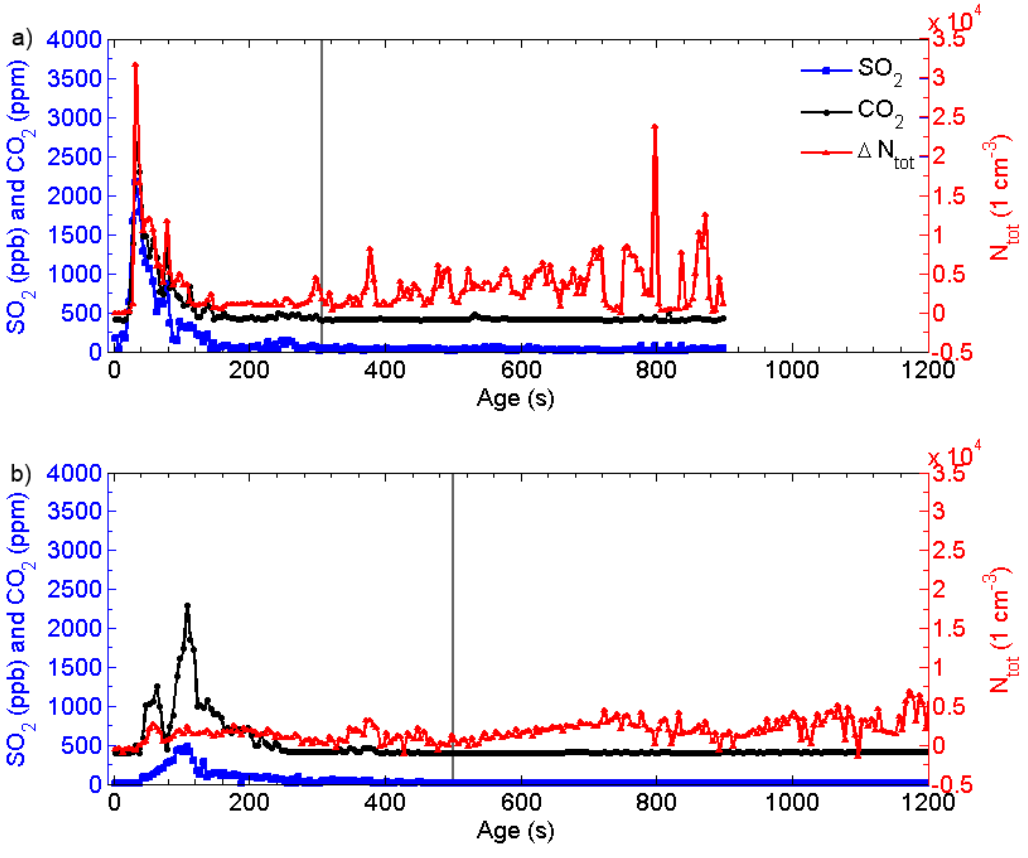

Figure 3. Concentrations of power plant flue gas components measured by instrument installed in to the helicopter as a function of plume age; "FGD+FF off" on the left and "FGD+FF on" on the right. SO_2 (ppb, black line) and CO_2 (ppm, blue line) concentrations on the left axes and total particle number concentration ΔN_{tot} (1 cm^{-3}, red line, from CPC) on the right axes. The ΔN_{tot} is calculated using the ~~closest~~ background value calculated upwind side of the stack ($CO_{2,bg}$ was 403 ppm and $SO_{2,bg}$ 2-8 ppb). The grey vertical lines denote 2 km distance from the stack in "FGD+FF on/off" cases. The presented results are 5 second median values.

~~at 350 sec in "FGD+FF on" case and at 250 seconds (SO_2, CO_2 and N_{tot}) in "FGD+FF off" case (Figure 3). The moderate increase in "FGD+FF on" case can be seen in EEPS data (Figure 4) but not in "FGD+FF off" case. To authors knowledge the moderate peaks cannot be explained by additional external emission sources because there should not be any sources at the same altitude in the flight directions (Figure 1) or upwind of the plume direction. Thus, the increased concentrations seem to be caused by occasionally different plume mixing.~~ In general, taking into account the fact that there is no comprehensive measurement of the primary precursor matrix (only [SO_2] is measured), the primary precursor matrix might include low-volatile organics and SO_3 which can increase the probability of new particle formation. Due to the increasing trend in particle concentration, some estimation about ~~nucleation~~ formation rates can be calculated. Depending on the plume age the mean ~~nucleation~~ formation rates calculated from the data shown in Figure 3 depended on the plume age being for "FGD+FF off" case 0–81 cm^{-3} s^{-1} and for "FGD+FF on" case 0 cm^{-3} s^{-1} to 18 cm^{-3} s^{-1} (~~average change in~~ mean slope of increasing total particle number concentration at 400–482 s and 500–692 s).

~~The particle number size distribution calculated from EEPS data as a functions of plume age. Measurement was made with the EEPS installed to helicopter. The results are calculated 10 second moving median values.~~

~~Figure 4 shows the flue gas plume particle number size distribution as a function of plume age.~~ ~~Distributions~~ Particle size distributions, shown in SI5, were calculated from the EEPS data measured from the helicopter in both "FGD+FF on/off" situations as 10 second moving median method. ~~In Figure 4 the freshly emitted plume~~ The particle size distribution in the "FGD+FF off" case ~~is changing in same ages than N_{tot} concentrations in Figure 3. The particle size distribution~~ had a mode around 80 nm, which refers to the solid particle median diameter measured with the SMPS from the flue gas in the stack. ~~Figure 4 indicates similar dilution profile for particles, if N_{tot} is calculated from EEPS data, than the dilution was for CO_2 and SO_2 in Figure 3. The comparison between~~ The particle size distribution measurement made by using the EEPS (SI5) supports the results for total particle number measurement made by the CPC (Figure 3)~~and EEPS particle size distribution (Figure 4) shows that~~, i.e. in terms of particles the flue gas is diluting in 0–300 seconds in "FGD+FF off"~~and 0–550 seconds in "FGD+FF on" and after that more small particles (and some larger particles) are detected in both cases~~. In addition, the particle size distributions measured by the EEPS indicates slight increase of nanoparticle concentrations during the dilution and dispersion of the flue gas in the atmosphere. Although, EEPS total particle number concentration cannot be compared to total concentration of CPC because Levin et al. (2015) showed that EEPS total particle number concentration is not comparable with a CPC. Further, the Figure ~~4~~ in SI5 the EEPS particle size distribution data is noisy and based on Awasthi et al. (2013) can show maximum of 67 % wrong compared to SMPS.

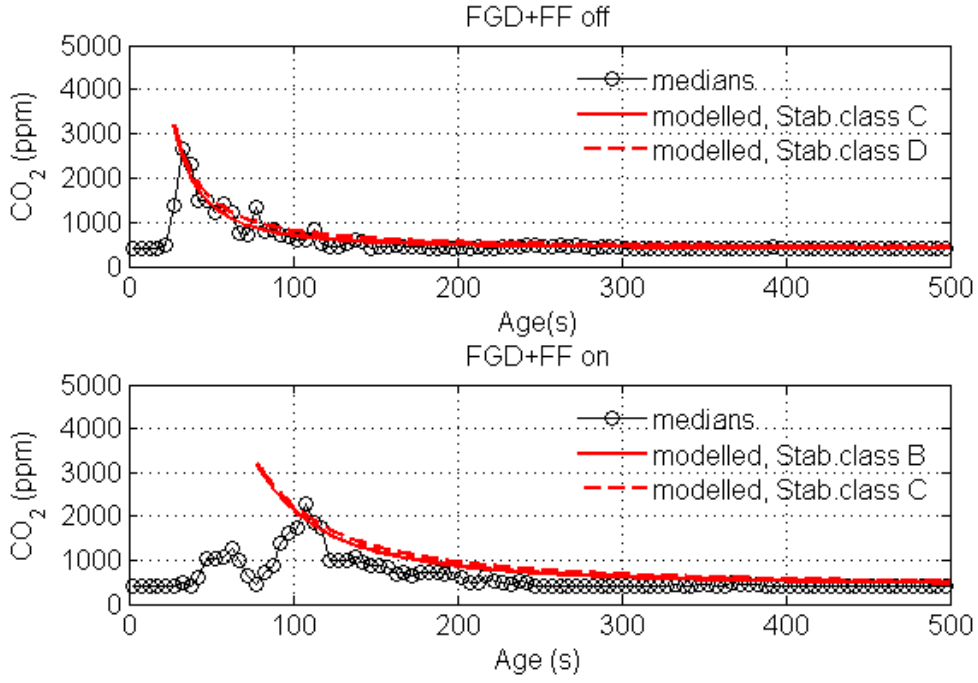

Figure 4. Comparison of measured and modelled CO_2 concentrations. Median of measured values are shown with black (circle) symbols along with the standard deviations. Dashed and dotted red lines correspond to model results for stability classes 'b' and 'c' (~~above~~top panel) and 'c' and 'd' (~~below~~bottom panel), respectively. The correlation coefficients between the model and the measurements are shown in Table **??**

3.3 Model Calculations: Modelled vs measured CO_2 concentrations

The validity of the Gaussian plume model was tested against CO_2 measurements from the plume. Median CO_2 concentrations were calculated using the measurement data at a five seconds interval separately for the "FGD+FF on/off" cases, and the locations of the peak CO_2 concentration (tmax, $[CO_{2,max}]$) were identified from the resulting time series. The value C_0 was chosen to eq. **??** so that the modelled CO_2 concentration, ~~$\hat{C}_{CO2}$~~$\hat{C}_{CO2}$, was around $[CO_{2,max}]$ when $t = t_{max}$. The choice of C_0 was made in this manner rather than initializing the model to use the stack concentrations due to the following two reasons. First, Gaussian plume model does not yield reliable results close, i.e. within a few tens of meters, to the source (Arya, 1995). Second, the comparison of the results near (first 10–50 seconds) the source is problematic because the helicopter was not located at the plume centerline during the initial stages of the measurements.

Comparison of the measured and modelled CO_2 concentrations is shown in Figure ~~5.~~ 5 and in Table **??**. The chosen stability classes were 'b' and 'c' as well as 'c' and 'd' for the "FGD+FF on" and "FGD+FF off" cases, respectively, corresponding to the stability conditions ranging from unstable to neutral (Pasquill, 1961). As can be seen, the model reproduces the observed trends rather

Table 2. Comparison between modelled CO_2 concentration and measured CO_2 concentration, and comparison between SO_2 measured from the atmosphere and Gaussian model diluted SO_2. Mean relative error (MRE) and correlation coefficients (R^2) were calculated between measured and modelled concentrations.

		CO_2		SO_2	
case	stab.class	MRE (%)	R^2	MRE (%)	R^2
"FGD+FF off"	c	5	0.97	131	0.95
	d	25	0.97	322	0.96
"FGD+FF on"	b	29	0.87	291	0.84
	c	40	0.87	413	0.85

well, in particular for the "FGD+FF off" case, while the model tends to slightly overestimate the observed concentrations for the "FGD+FF on" case. The modelled and measured concentrations were within one standard deviation in general. Mean relative error (MRE) and correlation coefficients (R^2) were calculated between the measured and modelled ~~values. For the "FGD+FF off" case, MREs were between 5 and 25%, depending on the stability class, and R^2 around 0.97, respectively. Corresponding values were between 29 and 40% (MRE) and around 0.86 (R^2) for the "FGD+FF on" case~~concentrations for CO_2. In order to further investigate the performance of the model, comparison was made between measured ~~and modelled~~ SO_2 and Gaussian model diluted SO_2 concentrations, shown in SI6. The results showed that the model consistently overestimates the SO_2 concentration in the plume, typically by a factor between 3 and ~~5~~4, compared to the measured values. This difference could be partly explained by the oxidation of SO_2 because it is not taken into account by the model. ~~For SO_2 measurement and model comparison, the values of MRE varied between 271–578% ("FGD+FF off" case) and between 291–413% ("FGD+FF on" case), depending on the stability class. Also,~~ However, this discrepancy between MRE's and R^2 ~~was 0.93 and 0.90 for "FGD+FF off" and"FGD+FF on" cases, respectively. However, this discrepancy~~ does not affect the model performance as the measured SO_2 concentrations, instead of ~~modeled~~modelled, were used in the plume model simulations.

3.4 Model Calculations: Nucleation and new particle formation

Modelled and measured CO_2 concentrations showed that the model reproduced the observed dispersion of the plume relatively accurately. Thus the model was applied to calculate [NO_x], [OH], and [H_2SO_4] which were needed to investigate possibility of new particle formation in the plume. These results are summarised in Figure 6. It is seen that sulphuric acid concentrations exponentially increase during the initial stages of the simulation and then reach constant concentration around $1{\cdot}10^6$ and $1{\cdot}10^7$ cm^{-3}, a range which is comparable also with the atmospheric observations of [H_2SO_4] (Mikkonen et al., 2011) formation. Mikkonen et al., (2011), have reported that H_2SO_4 concentrations varied between $1.86{\cdot}10^5$ – $2.94{\cdot}10^6$ molec cm^{-3}, and Sarnela et al., (2015) reported

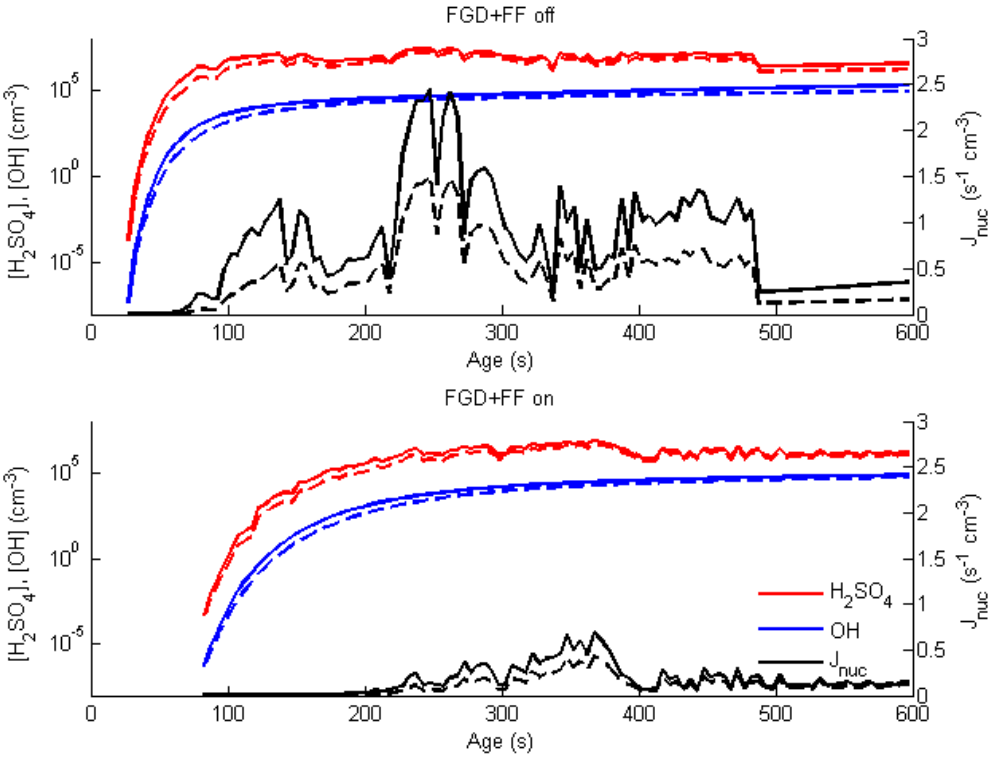

Figure 5. Time development ~~Blue lines –~~of [H_2SO_4] ~~,~~(red lines~~–~~), nucleation rate ~~,~~(black lines~~–~~), [OH] (blue lines) (cm^{-3}). Dashed and dotted red lines correspond to model results for stability classes '~~b~~c' and '~~e~~d' (~~above~~top panel) and '~~e~~b' and '~~d~~c' (~~below~~bottom panel), respectively.

[H_2SO_4] concentrations 0.38–0.75 ppbv for Finnish industrial and non-industrial area. More H_2SO_4 is formed in the "FGD+FF off" case because of higher primary SO_2 emission compared to the "FGD+FF on" case.

Initially, OH concentrations are lowered by large concentrations of NO_x which subsequently decreases during plume ageing. NO_x reduction leads to increases in [OH] and [H_2SO_4]. While the [OH] increased consistently during the simulations, [SO_2] decreased because of dilution. Due to these opposed trends, the production term for the sulphuric acid, ~~$k_1 \times SO_2 \times OH$~~in equation **??**, did not change greatly during the later stages of the simulations. Moreover, the condensation sink (CS) diluted rapidly to its background value, which was around $1 \cdot 10^{-2}$ s^{-1}. These facts explain why the modelled sulphuric acid concentrations, calculated with ~~$H_2SO_4 = k_1 \times SO_2 \times OH/CS$~~equation **??**, did not change notably after the initial, rapid increase.

The modelled nucleation rate J_{nuc} is directly proportional to the sulphuric acid concentration and hence the trends in [H_2SO_4] are directly reflected in J_{nuc} (Figure 6). ~~The mean values of J_{nuc} were around 0.4 or 0.7 $cm^{-3}s^{-1}$, in the "FGD+FF off" case and 0.1 or 0.17 $cm^{-3}s^{-1}$ in the "FGD+FF on"~~

case, both nucleation rates dependent on the stability class. Furthermore, apparent particle formation rate were calculated Furthermore, in our measurements the particles were detected at the lowest CPC detection limit which was 2.5 nm, J25$J_{2.5}$. According to the scheme applied here , (see equations ?? and ??), the fraction of freshly nucleated particles that survive into detectable sizes depends mainly on their growth rate (GR) and on the condensation sink (CS). The average given by the model GRs were 0.34 or 0.19 nm/h in the "FGD+FF off" case, and 0.07 or 0.04 nm/h in the "FGD+FF on" case ; both cases are depending on the stability classfor the two stability class scenarios. These values are clearly smaller than estimations for atmospheric observations atmospheric GR observations in urban areas (e.g. Kulmala Stoltzenburg et al., 2001)and thus, 2005). As a lower GR leads to a lower surviving fraction, we conclude that the modelling results do not explain the observed particle formation in the flue gas plume.

A series of additional calculations were performed in order to investigate the sensitivity of the results to the values of the key input parameters. First, J_{nuc} is proportional to the constant A whose exact value is not accurately known, and this uncertainly translates directly into the calculated nucleation rates. A sensitivity analysis was made for the nucleation model in order to evaluate the sensitivity of nucleation rates to the value of A (shown in Table **??**). In these calculations, a value of $1{\cdot}10^{-6}$ was chosen for A which is an order of magnitude higher than in base case simulations. The choice of the value was based on the study of Sihto et al. (2006) who investigated NPF events occurring on boreal forest. As can be seen, increased value of A is not sufficient alone to explain observed new particle formation. A second source of uncertainty is terms of the sulfuric acid concentration which was calculated using a rather simple scheme (see section 2.1.1). Increases in $[H_2SO_4]$ leads to both increased Jnuc J_{nuc} and GR and ultimately to larger J25$J_{2.5}$. Results displayed in Table **??** show that J25 $J_{2.5}$ is more consistent with observations when $[H_2SO_4]$ is increased five or ten-fold and when A is set equal to $1{\cdot}10^{-6}$ like in Sihto et al. (2006). Therefore, underestimation of $[H_2SO_4]$ may explain the discrepancy between the obeservations and base case model results. This might caused by underestimation of [OH] or overestimation of CS. Regarding the modeled OH concentrations, it can be noted that they are relative low, reaching values of around $1{\cdot}10^5$ cm^{-3} by the end of the flights. In comparison, concentrations of around $1{\cdot}10^6$ cm^{-3} have been reported during the daytime around noon in various atmospheric environments (Hofzumahaus et al., 2009; Petäjä et al., 2009). , $0.26{\cdot}10^6$ molec cm^{-3} in Mace Head (Berresheim et al., 2002), and $1{\cdot}10^6$–$2{\cdot}10^7$ molec cm^{-3} in Atlanta (Kuang et al., 2008). Relative low modeled OH concentrations can be explained by high NO_x concentrations which were calculated to decrease consistely from several tens of ppm down to around 200 ppb during the flights (not illustrated here). Such high concentrations of NO_x are consistent with low [OH] (see Figure 1 in Lonsdale et al., 2014). It could be thus speculated that model underestimates $[H_2SO_4]$, and consequently rate of new particle formation, due to overestimation of $[NO_x]$. Moreover, it should be noted that neither SO_3 nor low-volatile organic vapours that might have been present in the measured flue gas were not accounted for in the modeling study. Previous

Table 3. Sensitivity analysis made for number of particles formed with diameters above 2.5 nm during the flight (1 cm^{-3} ~~(600 s)~~ $^{-1}$) in the atmosphere with different values of A and $[H_2SO_4]$. The $[H_2SO_4]$ is calculated based on the measurement results and scaled up to test faster nucleation rate for both "FGD+FF on" and "FGD+FF off" cases and stability classes (sc).

		A=1 · 10^{-7} s^{-1}				
	sc	1·$[H_2SO_4]$	1.25·$[H_2SO_4]$	1.5·$[H_2SO_4]$	2·$[H_2SO_4]$	5·$[H_2SO_4]$
"FGD+FF off"	b	~~6.02~~1.00·$10^{~~-2~~-4}$	~~3.21~~5.36·$10^{~~-1~~-4}$	~~1.044.97~~1.73·$10^{~~2~~-3}$	~~1.04~~8.29·$10^{~~3~~-3}$	0.289
	c	~~3.66·10^{-4}~~0	~~4.70·10^{-3}~~0	~~2.68·10^{-2}~~0	~~2.59~~4.32·$10^{~~-1~~-4}$	~~2.87~~4.78·$10^{~~1~~-2}$
"FGD+FF on"	c	0	0	0	0	~~2.56~~4.27·$10^{~~-1~~-4}$
	d	0	0	0	0	~~5.20~~0
		A=1 · 10^{-6} s^{-1}				
	sc	1·$[H_2SO_4]$	1.25·$[H_2SO_4]$	1.5·$[H_2SO_4]$	2·$[H_2SO_4]$	5·$[H_2SO_4]$
"FGD+FF off"	b	~~0.63.21~~1.04~~1.00~~·$10^{~~1~~-3}$	~~4.97~~5.36·$10^{~~1~~-3}$	1.73·$10^{~~3~~-2}$	~~1.04~~8.29·$10^{~~4~~-2}$	2.89
	c	~~3.66·10^{-3}~~0	~~46.80·10^{-2}~~0	~~0.26~~~~82.59~~~~2.87~~4.47·$10^{~~2~~-4}$	~~2.66~~4.32·$10^{~~3~~-3}$	0.48
"FGD+FF on"	c	0	0	0	~~2.3·10^{-4}~~0	~~2.56~~1.14.27·$10^{~~2~~-3}$
	d	0	0	0	0	~~0.05~~20

studies suggest that these exhaust compounds may increase also the formation rate of nucleation particles (Pirjola et al., 2015; Ehn et al., 2012; Arnold et al., 2012) which may also explain the discrepancy between measurements and model calculations. Regarding the estimation of the value of CS, it should be noted that its values were taken from the field site measurements located nearby rather than from in-situ measurements. Therefore it can be speculated that actual CS values were lower than those used as input to the model which cause additional uncertainties.

3.5 Discussion

Each power plant (over 50 MW) in EU has emission limits for SO_2, NO_2, and particle mass concentrations, for ~~this~~ the studied power plant the limits are 600 mg Nm^{-3} (210 ppm), 600 mg Nm^{-3} (290 ppm), and 50 mg ~~m~~Nm^{-3}~~n~~, respectively. Comparison ~~between~~ of the results in Table 1 ~~results with the emission limits above~~ with these emission limits shows that the emissions were clearly below these limits when the power plant operation was normal ~~e.g.~~ ("FGD+FF on"). It was observed that these low emissions can be achieved by properly working flue gas cleaning systems. In addition to primary emissions, flue gas cleaning systems seemingly affect also the ~~amount of H_2~~compounds which can act as precursors for new particles; e. g. $SO_{~~4~~}$~~of new aerosol particles, such as SO_2~~ ~~which tends to oxidate~~ tends to oxidize in the atmosphere to SO_3 and, further, to form H_2SO_4 which can nucleate or condensate to particle phase. This study shows clearly the importance of flue gas cleaning technologies, and underlines the proper usage of the technologies when the atmospheric pollution is

discussed in terms of coal combustion. E.g. according to Huang et al. (2014) in Xi'an and Beijing 37% of sulphate in the atmospheric particles is emitted from coal burning.

~~The~~ In this study the power plant plume ~~dilutes~~ diluted to background levels in ~~200 seconds~~2 km (200–400 seconds) which is faster than ~~indicated~~ in other in-flight measurements (Stevens et al., 2012; Junkermann et al., 2011). This difference may be because the dilution of plume and other processes are affected by source strength, background concentrations, and meteorology (Stevens et al., 2012). We observed that while SO_2 and CO_2 were already diluted to background levels the effect of the source to aerosol concentration was still clearly distinguishable after 2 km. In our study, we collected high-time-resolution data close to the power plant stack, which enable us to model the plume dilution on a detailed scale. From this, we were able to observe that while SO_2 and CO_2 were already diluted to background levels at a distance of 2 km – in agreement with the dilution modeling – the effect of the source to the aerosol number concentration was distinguished at distances >2 km. We attribute this to nucleation taking place in the ageing plume.

According to modelling results of Stevens et al. (2012), atmospheric new particle formation via coal combustion originated sulphuric acid nucleation begins at ~~5~~ 1 km distance from the source whereas the sulphuric acid formation begins right after emission. ~~Experiments of this study indicates that the~~ Our study therefore supports this previous modelling work by showing that nucleation may take place in the aged plume and being the most effective after 400 seconds, corresponding approximately 2 km distance from the emission source in atmosphere.

~~Also this distance is significantly less than 5 km distance indicated by Stevens et al. (2012). Thus, this study indicates that atmospheric nucleation in power plant plumes takes place faster than the models and measurements have suggested before. Also, it has been known that new particles form in sulphur-rich plumes (Junkermann et al., 2011), but this study shows that nucleation can take place in lower SO_2 concentrations. In general, the particle number concentrations in the urban atmosphere may be underestimated due to particle formation in power plant plumes.~~

In the light of the new results authors would like to distinguish the primary particle emission from the newly formed particle emission because those particles have different effects on the atmosphere and different formation mechanisms. Comparing primary particle emission with newly formed particle emission, the effects of different particles in the atmosphere could be taken into account more precisely in aerosol models or air quality assessment.

For instance, ~~in the plume for "FGD+FF off" case rough estimates~~ rough estimates for particle number emission factors can be calculated ~~for the particle number emission (from CPC, Figure 3) per grams of~~ by comparing the measured particle number concentration with the simultaneously measured CO_2 concentration of the flue gas plume (see e.g. Saari et al. 2016). By utilizing this method, for particles existing in the ~~plume~~ flue gas plume in ages of 25–55 seconds the emission factor in respect of CO_2 was $2.0 \cdot 10^{10}$ (g CO_2)$^{-1}$ and in ages over 400 seconds $8 \cdot 10^{10}$ (g CO_2)$^{-1}$ ~~and~~in the "FGD+FF off" case. Similarly, in the "FGD+FF on" case ~~between 55–85 seconds~~ the

emission factors were $4{\cdot}10^9$ (g CO_2)$^{-1}$ ~~and after 500 seconds~~ (for aerosol dispersed 55–85 seconds in the atmosphere) and $3.74{\cdot}10^{10}$ (g CO_2)$^{-1}$ (for aerosol dispersed more than 500 seconds in the atmosphere). In comparison, the primary emissions were $1.75{\cdot}10^{10}$ (g CO_2)$^{-1}$ for "FGD+FF off" case and $8.0{\cdot}10^6$ (g CO_2)$^{-1}$ for "FGD+FF on" case. Thus, new particle formation can increase the real atmospheric particle number emissions even several orders of magnitude. It should be noted that the particle formation depends strongly on the plume age, [SO_2] and primary particle concentrations, and it is possible that there are some low-volatile organics or SO_3 present at the plume affecting the nucleation.

~~Coal combustion is harmful for climate due to the CO_2 emission. However, also atmospheric particles affect the climate having either cooling or warming effect depending on their chemical and physical characteristics. It is known, that soot or black carbon containing particles have a warming effect on climate. This study indicated that most of~~ Our observations show that the number of secondary particle formed in the flue gas plume can be several orders of magnitude higher than the primary particles directly emitted from the ~~particles originated from coal combustion are formed in the atmosphere. Based on that knowledge, it can be assumed that the formed particles are more scattering than absorbing. Also, Frey~~ flue gas duct. The formation can be observed already at a distance of ca 2 km from the stack; this distance is significantly lower than the grid size used in many atmospheric models, which demonstrates the need for subgrid parameterizations for power plat-originated secondary particles. Such a parameterization does already exist (Stevens et al.~~(2014)have shown that primary emission of the coal-fired power plant has a scattering effect, at least when compared to other combustion originated primary particles. This study gives new insights when the effects of coal combustion are studied in a global scale. Finally, the results help to understand the formation of atmospheric particles in polluted areas, such as India and China~~, 2013), but it does not account for different types of sulphur removal technologies such as semi-dry desulphurization, wet desulphurization. Determining the effect of different removal technologies on power plant secondary aerosol production would increase the accuracy of particle loading predictions for regional air quality and global models.

4 Conclusions

Emissions of a coal-fired power plant into the atmosphere were studied comprehensively, for the first time, by combining direct atmospheric measurements, measurements conducted in the power plant stack, and modelling studies for atmospheric processes of flue gas plume. The stack measurements were made to estimate the effectiveness of flue gas cleaning technologies, such as filtering and desulphurization. It was shown that the flue gas cleaning technologies had a great effect on the SO_2 and total particle number concentrations in the primary emission. SO_2 concentration was reduced to fifth of "FGD+FF off" situation compared to "FGD+FF on" situation and the total non-volatile particle

number concentration was reduced by orders of magnitude. Similar trend in primary emission reduction was detected in the atmospheric measurements. In addition, the reduction in primary emissions affects directly the concentrations of gaseous precursors (SO_2) for secondary particle formation in the atmosphere.

It was observed that the flue gas dilutes to background concentrations in 200–300 seconds. This dilution time scale is faster than reported in previous studies. However, the concentration profiles also showed an increase in particle number concentration in an aged flue gas, dilution and dispersion processes.

To validate the dilution time scale, a Gaussian model was used to calculate the dilution in the atmosphere taking into account the primary emission and weather conditions. The Gaussian model confirms the dilution time scale, and the dilution ratio could be used to calculate the theoretical maximum values for different components in the flue gas plume. Weather conditions and theoretical maximum value for [NO_x] was used to calculate the [OH] formation rate and further [H_2SO_4] formation rate. These were calculated because the measurement results showed an increase in particle number concentrations in the flue gas plume during the dilution process. The modelling results for [H_2SO_4] formation rate support the hypothesis of sulphuric acid formation, but the sulphuric acid formation itself does not totally explain the increase in the total particle number concentration, therefore, e.g. low-volatile organics may excist on the flue gas plume. The sensitivity analysis of the [H_2SO_4] formation showed that the atmospheric parametrization is not enough to explain the processes in the flue gas plume.

Comparison between the primary particles and newly formed particles ~~, calculated based on the atmospheric results, show~~ show that in the flue gas plume of coal-fired power plant the concentration of newly formed atmospheric particles can be several orders of magnitude higher than the primary particles from the flue gas duct~~. This is the reason why the newly formed particles should be taken into account when discussing power plant emissions in the future. The formation of these particles in the power plant plumes should be properly parametrized to implement power plants more efficiently e. g. in air quality and climate models.~~

~~It is widely known that CO_2 emissions are harmful for the climate. However, the CO_2 emission is not the only one to have effects on the climate. Other anthropogenic gases can increase the climatic effects. Particles contribute the climate negatively and positively depending on the particle properties in the atmosphere. This study linked with the knowledge for other atmospheric studied indicates that the atmospheric particle formed in flue gas plumes are scattering more light than absorbing and, thus adding the cooling effect of the primary emissions of a coal-fired power plant. In addition, this study brings new insight to the atmospheric effects of coal combustion, as well as helps to understand formation of atmospheric particles in polluted areas~~; therefore, they should be considered when discussing emissions of power production. Including the effect of varying flue gas cleaning

technologies in parameterizations of power-plant-originated secondary particles is a necessary step in understanding their importance.

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