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

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Received: 8 December 2015 – Published in Atmos. Chem. Phys. Discuss.: 5 February 2016
Revised: 24 May 2016 – Accepted: 30 May 2016 – Published: 15 June 2016

Abstract. Atmospheric emissions, including particle number and size distribution, from a 726 MWth coal-fired power plant were studied experimentally from a power plant stack and flue-gas plume dispersing in the atmosphere. Experiments were conducted under two different flue-gas cleaning conditions. The results were utilized in a plume dispersion and dilution model taking into account particle formation precursor (H2SO4 resulted from the oxidation of emitted SO2) and assessment related to nucleation rates. The experiments showed that the primary emissions of particles and SO2 were effectively reduced by flue-gas desulfurization and fabric filters, especially the emissions of particles smaller than 200 nm in diameter. Primary pollutant concentrations reached background levels in 200–300 s. 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 (H2SO4 from SO2 oxidation) concentrations remain relatively constant. In addition, results indicate that flue-gas nucleation is more efficient than predicted by atmospheric aerosol modelling. In particular, the observation of the new particle formation with rather low flue-gas SO2 concentrations changes the current understanding of the air quality effects of coal combustion. The results can be used to evaluate optimal ways to achieve better air quality, particularly in polluted areas like India and China.

1 Introduction

On the global scale, nearly 40 % of annual production of electricity is covered by coal combustion (EU, 2014). In addition to CO2 emissions, known to have climatic effects, coal combustion causes emissions of other harmful pollutants like NOx, SO2 and particulate matter, all decreasing the air quality and increasing health-related risks but also affecting climate directly and indirectly. For instance, SO2 affects the climate indirectly because it tends to oxidize in the atmosphere and form H2SO4, which affects particle formation. Coal-combustion-related air quality problems exist, especially in developing countries like China (Huang et al., 2014), where power production is not always equipped with efficient flue-gas cleaning technologies. However, with proper combustion and flue-gas cleaning technologies the fine particle emissions of coal combustion can be decreased to a very low level and the emissions of gaseous pollutants other than CO2 can also 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 desulfurization unit (FGD) have been
reported by Frey et al. (2014): the emission for particle mass (PM$_1$) was 0.18 ± 0.06 mg MJ$^{-1}$ and for fine particle number 2.3 × 10$^4$ ± 4.0 × 10$^3$ MJ$^{-1}$. However, it can be expected that particle emissions and characteristics such as particle size are highly dependent on technologies used in power production. Only a 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 desulfurization chemicals. Interestingly, sulfate particle emissions from coal combustion with proper cleaning technologies can restrain global warming due to a cooling effect of the particles (Frey et al., 2014; Charlson et al., 1992; Lelieveld and Heintzenberg, 1992).

Due to the emission limits of power plants, driven by the need for a 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 desulfurization (FGD) (Srivastava and Jozewicz, 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, for particle emission, ESP typically removes 99 % (Helble, 2000) of fine particles. Further, Saarnio et al. (2014) showed that a desulfurization plant with fabric filters removes up to 97 % of fine particles. A combination of these techniques would then remove 99.97 % of fine particle emissions formed in combustion. However, particle emission as well as the effects of technologies can differ 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 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 aircraft by measuring long-distance crosswind 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 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 that the secondary particle formation begins in a 2 h old plume. A study by Brock et al. (2002) has focused on 0 to 13 h old power plant plumes. However, Brock et al. (2002) do not report particle number concentrations for fresh flue gas. Crosswind profiles shown in the study of Stevens et al. (2012) were at distances from 5 km to a little over 50 km, 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 also made a few crosswind profiles of the studied plume.

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. desulfurization plant and fabric filters (later referred to 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.

2 Experimentation

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$_x$), situated at the front wall of the boiler. The properties of coal used in this study are listed in Table S1 in the Supplement. Combustion releases flue gases that are cleaned in electrostatic precipitator (ESP), semi-dry desulfurization 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 in 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 m above sea level. The flue-gas temperature inside the duct was 78 ± 2°C in normal operation conditions and 130 ± 13°C during FGD + FF off. The flue-gas plume concentrations were measured with a helicopter equipped with aerosol instruments. The flying altitude of the helicopter was 150 m above ground level or higher, which corresponds to the lidar (Halo Photonics Streamline Doppler lidar with full-hemispheric scanning capability, Pearson et al., 2009) (Fig. S2) 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, the flue-gas plume consisted of both the cleaned flue gas and the flue gas cleaned by ESP. This has to be kept in mind during the analysis of atmospheric measurements.

The measurements were made on 24 March 2014 in two separate 1 h periods (see specific times from Fig. S2, the black rectangles; the first illustrates FGD + FF on and the lat-
ter FGD + FF off). Weather conditions were stable during the study. The wind direction and speed were 216 ± 5.51° (based on lidar data) and 6.5 m s⁻¹ in FGD + FF off and 220 ± 6.25° and 4 m s⁻¹ in FGD + FF on. The marine boundary layer height was 246–258 m and the planetary boundary layer heights were 360–530 m. However the calculations were made within the marine boundary layer because the flue-gas plume did not rise above it. The background aerosol concentrations for each measured gaseous component were 403 ppm for CO₂ and less than 2–8 ppb for SO₂. The range of ambient temperature was 6.6–6.9 °C, the global radiation was 347–466 W m⁻² and the visibility was 29 043–36 000 m (see standard deviations from Table S2).

The instrument installations in different locations are shown in Fig. S3. The sampling of flue gas in the stack was performed with a 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 analysed using the following instruments: Condensation Particle Counter (CPC3776; TSI Inc., Agarwal and Sem, 1980), Electrical Low Pressure Impactor (ELPI; Dekati Ltd., Keskinen et al., 1992), Scanning Mobility Particle Sizer (SMPS; Wang and Flagan, 1990) 0.6/6 standard L min⁻¹ (DMA3071, CPC3775 TSI Inc.) and gas analysers for diluted CO₂ (model VA 3100, Horiba) and NO, NO₂ and NOx (model APNA 360, Horiba). Measurement data were also received from a normal operation monitoring of the emissions, including raw flue-gas SO₂, NOx, CO₂ 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 Fig. S3. Natural dilution causes rapid changes in concentrations, thus high measurement frequency equipment was used in the helicopter. CPC3776 (TSI Inc.) was installed to measure the total particle number concentration, whereas the Engine Exhaust Particle Sizer (EEPS, TSI Inc., Mirme, 1994) measured the particle number size distribution at 1 Hz sampling frequency from 5.6 to 560 nm. Gas concentrations for CO₂/CH₄/H₂O (Cavity spring-down spectrometry Picarro model G1301-m) CO₂/CH₄/H₂O flight analyser) and SO₂ (Thermo Scientific Inc. model 43i SO₂ analyser, with 5 s response time) were measured continuously with 1 Hz frequency (see more details in Table S3).

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

![Figure 1. Helicopter flight routes. The wind blew at an 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 (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.](image)

### 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, Cᵢ, emitted from a point-like source, can be expressed as follows:

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

(1)

Here, x, y and z are the spatial coordinates, aligned so that the x axis corresponds to the wind direction and H is the height at which i is emitted (stack height). Also, Qᵢ is the emission rate of i at the source, U is the mean wind speed and \(\sigma_z\) as well as \(\sigma_y\) 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 centre line of the plume, the value of U was set to constant and was equal to the average wind speed during the flights. Finally the value of z was set equal to the stack height (150 m).
It is worth noting that the background concentration of \( i \) is zero according to Eq. (1): \( C_i \rightarrow 0 \) when \( z \rightarrow \infty \) or \( y \rightarrow \pm \infty \). 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 order to account for such cases, the following equation was used instead of Eq. (1):

\[
\hat{C} = C_\infty + \frac{C_0 - C_\infty}{C_0} \times C_i,
\]

(2)

where \( C_\infty \) is the background concentration of \( i \), and \( C_0 \) is its concentration at the source. It can be readily shown that Eq. (2) is a solution to the advection–diffusion equation underlying Eq. (1). Also, it is easily verified that \( \hat{C} \rightarrow C_\infty \) when \( z \rightarrow \infty \) or \( y \rightarrow \pm \infty \). Finally, the value of \( Q_i \) in Eq. (1) was chosen so that \( \hat{C} \rightarrow C_0 \) when \( z \rightarrow H \) and \( x, y \rightarrow 0 \).

An important output of the model is the dilution ratio of the flue-gas plume, DR, which is calculated based on Eq. (3).

\[
DR(t) = \frac{[CO_2(t)] - [CO_2,\infty]}{[CO_2,stack] - [CO_2,\infty]}
\]

(3)

In Eq. (3) \([CO_2(t)]\) and \([CO_2,\infty]\) are the modelled CO2 concentration at time \( t \) and the CO2 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 for the particles 2.5 nm in diameter were calculated using the parameterization developed by Lehtinen et al. (2007) presented in Eq. (4). The key input parameters for the model are the nucleation rate \( J_{nuc} \), the particle growth rate \( (GR) \) and the coagulation sink, of which the coagulation sink describes clusters that are removed via coagulational scavenging (CoagS). The parameter \( J_{nuc} \) is calculated based on the estimated sulfuric acid concentrations as a function of plume age as detailed below, and the particle growth rates are calculated by assuming growth only via irreversible condensation of sulfuric 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 \(-1.6\).

\[
J_s = J_{nuc} \times \exp \left( -\gamma \times d_1 \times \frac{\text{CoagS}(d_1)}{\text{CS}} \right)
\]

(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; Stevens and Pierce, 2013).

\[
J_{nuc} = A \times [H_2SO_4]
\]

(5)

In Eq. (5) \( A = 1 \times 10^{-7} \text{ s}^{-1} \) or \( A = 1 \times 10^{-6} \text{ s}^{-1} \) and \([H_2SO_4]\) (cm\(^{-3}\)) is the sulfuric acid concentration. The value of \( A = 1 \times 10^{-7} \text{ s}^{-1} \) was chosen according to the study by Stevens et al. (2012) and Stevens and Pierce (2013). The initial 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\(_2\)SO\(_4\) is condensation onto the particle surfaces. When steady-state is assumed, the \([H_2SO_4]\) can be calculated from Eq. (6).

\[
[H_2SO_4] = k_1 \times \frac{[SO_2] \times [OH]}{\text{CS}}
\]

(6)

In Eq. (6) \( k_1 \) is the reaction constant between OH and SO\(_2\) (Table B.2 in Seinfeld and Pandis, 2006). 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 shown in Eq. (7).

\[
\text{CS} = \frac{\text{CS}_{\text{stack}}}{\text{DR}(t)} + \text{CS}_\infty \times \left( 1 - \frac{1}{\text{DR}(t)} \right)
\]

(7)

In Eq. (7) \( \text{CS}_{\text{stack}} \) is the condensation sink of aerosols measured in the stack, and \( \text{CS}_\infty \) 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 2 km 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. The 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 from Eq. (8).

\[
[\text{NO}_x(t)] = \frac{[\text{NO}_x,\text{stack}]}{\text{DR}(t)}
\]

(8)

In Eq. (8) \([\text{NO}_x,\text{stack}]\) 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 plants. To support this, the study of Pirjola et al. (2014) indicates that in the harbour area close to the power plant studied, 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 the 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\(_{\text{tot}}\)), 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, the SO₂ concentration decreased to nearly a fifth, the concentration of dust decreased by a factor of 50 and the Nₐₒₐ decreased by a factor of 4000. 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 a 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 was 2.15. Based on the measurements using the ELPI geometric mean aerodynamic equivalent diameter was 141 nm and GSD was 1.41 for FGD + FF off. The difference in mean diameter measured using the ELPI and the SMPS comes from the difference in size classification principles of these instruments and enables the determination of effective density of measured particles. The effective density 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 diameter indicates effective density larger than unit density for emitted particles (approximately 3.1 g cm⁻³). In comparison, Saarnio et al. (2014) used an effective density of 2.5 g cm⁻³ to convert the electrical mobility diameter measured using a SMPS to an aerodynamic diameter. When studying FGD + FF on, 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 samples from the stack were diluted with hot dilution air before the particle instruments and thus the particle number concentrations (Table 1) and particle size distributions (Fig. 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 lifetime 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

Figure 3 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 set-up (see Fig. S4). The data were 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 of 6.5 and 4.0 m s⁻¹ (lidar, Fig. S2). 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 Fig. 3 can be higher than shown here. The vertical lines denote the 2 km distance from the stack. Figure 3 shows the dilution timescale of the flue gas in terms of CO₂ and SO₂ in both operation conditions. The same trend in SO₂ and Nₐₒₐ concentrations as observed in Table 1 was measured by instruments installed in

---

**Table 1.** Flue-gas concentrations of CO₂, SO₂, NOₓ, O₂, total particle number (Nₐₒₐ), dust and flue-gas flow rate in the stack. Mean values (and standard deviation) are presented for both flue-gas cleaning conditions (FGD + FF on and FGD + FF off).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>FGD + FF off</th>
<th>FGD + FF on</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ (%)</td>
<td>9.92 ± 2.2</td>
<td>10.3 ± 0.96</td>
</tr>
<tr>
<td>SO₂ (ppbw)</td>
<td>243 000 ± 71 300</td>
<td>55 200 ± 14 600</td>
</tr>
<tr>
<td>NOₓ (ppmv)</td>
<td>252 ± 74</td>
<td>258 ± 65</td>
</tr>
<tr>
<td>O₂ (%)</td>
<td>6.16 ± 0.11</td>
<td>6.11 ± 0.10</td>
</tr>
<tr>
<td>Nₐₒₐ (cm⁻³)</td>
<td>(1.8 ± 0.2) × 10⁶</td>
<td>420 ± 640</td>
</tr>
<tr>
<td>Dust (mg Nm⁻³)</td>
<td>188 ± 82</td>
<td>4 ± 1</td>
</tr>
<tr>
<td>Flow (Nm³ h⁻¹)</td>
<td>(4.86 ± 0.20) × 10⁵</td>
<td>(4.65 ± 0.064) × 10⁵</td>
</tr>
</tbody>
</table>
An increase in total particle concentration can be seen in Fig. 3 after 400 s aged the flue-gas plume. This tendency can be seen in both flue-gas cleaning situations. Based on Fig. 3a, for the FGD + FF off situation, the background particle concentration was 1430 cm\(^{-3}\), after 200 s the concentration was at the background level and after 400 s it increased significantly, even up to an average level of 5000 cm\(^{-3}\). Based on CO\(_2\) measurements, the dilution of flue gas was practically complete at 200 s. Similarly, in the FGD + FF on situation after 500 s the particle concentration was slightly above background, after which it increased even up to 5000 cm\(^{-3}\) after 700 s. 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. 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 formation rates can be calculated. Depending on the plume age, the mean formation rates calculated from the data shown in Fig. 3 depended on the plume age being for FGD + FF off 0–81 cm\(^{-3}\) s\(^{-1}\) and for FGD + FF on, 0 to 18 cm\(^{-3}\) s\(^{-1}\) (mean slope of increasing total particle number concentration at 400–482 and 500–692 s).

Particle size distributions, shown in Fig. S5, were calculated from the EEPS data measured from the helicopter in both FGD + FF on/off situations as a 10 s moving median method. The particle size distribution in the FGD + FF off case 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. The particle size distribution measurement made using the EEPS (Fig. S5) supports the results for total particle number measurement made using the CPC (Fig. 3), i.e. in terms of particles the flue gas dilutes in 0–300 s in FGD + FF off. In addition, the particle size distributions measured by the EEPS indicates a 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, Fig. S5 shows that the EEPS particle size distribution data are noisy and, based on Awasthi et al. (2013), can show maximum of 67 % error compared to SMPS.

### 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 5 s
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.

<table>
<thead>
<tr>
<th>case</th>
<th>stab. class</th>
<th>CO$_2$ MRE (%)</th>
<th>$R^2$</th>
<th>SO$_2$ MRE (%)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FGD + FF off</td>
<td>c</td>
<td>5</td>
<td>0.97</td>
<td>131</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>d</td>
<td>25</td>
<td>0.97</td>
<td>322</td>
<td>0.96</td>
</tr>
<tr>
<td>FGD + FF on</td>
<td>b</td>
<td>29</td>
<td>0.87</td>
<td>291</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>40</td>
<td>0.87</td>
<td>413</td>
<td>0.85</td>
</tr>
</tbody>
</table>

interval separately for the FGD + FF on/off cases and the locations of the peak CO$_2$ concentration ($t_{\text{max}}$, $[\text{CO}_2\text{, max}]$) were identified from the resulting time series. The value $C_0$ was chosen for Eq. (2) so that the modelled CO$_2$ concentration, $C_{\text{CO}_2}$, was around $[\text{CO}_2\text{, max}]$ when $t = t_{\text{max}}$. 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, the Gaussian plume model does not yield reliable results close to the source, i.e. within a few tens of metres (Arya, 1995). Second, the comparison of the results near (first 10–50 s) the source is problematic because the helicopter was not located at the plume centre line during the initial stages of the measurements.

Comparison of the measured and modelled CO$_2$ concentrations is shown in Fig. 4 and in Table 2. The chosen stability classes were b and c for FGD + FF on and c and d for FGD + FF off, corresponding to the stability conditions ranging from unstable to neutral (Pasquill, 1961). As can be seen, the model reproduces the observed trends rather well, in particular for FGD + FF off, while the model tends to slightly overestimate the observed concentrations for FGD + FF on. 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 concentrations for CO$_2$. In order to further investigate the performance of the model, a comparison was made between measured SO$_2$ and Gaussian-model-diluted SO$_2$ concentrations, shown in Fig. S6 and Table 2. The results showed that the model consistently overestimates the SO$_2$ concentration in the plume, typically by a factor between 3 and 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. However, this discrepancy between MREs and $R^2$ does not affect the model performance as the measured SO$_2$ concentrations, instead of being 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 relativistically accurately. Thus the model was applied to calculate [NO$_x$], [OH] and [H$_2$SO$_4$], which were needed to investigate the possibility of new particle formation in the plume. These results are summarized in Fig. 5. It is seen that sulfuric acid concentrations exponentially increase during the initial stages of the simulation and then reach constant concentration around $1 \times 10^6$ and $1 \times 10^7$ мolec cm$^{-3}$, which is also comparable to the atmospheric observations of [H$_2$SO$_4$] (Mikkonen et al., 2011) formation. Mikkonen et al. (2011) reported that H$_2$SO$_4$ concentrations varied between $1.86 \times 10^5$–$2.94 \times 10^6$ мolec cm$^{-3}$ and Sarnela et al. (2015) reported [H$_2$SO$_4$] concentrations $4.4 \times 10^6$–$11.5 \times 10^7$ мolec cm$^{-3}$ for Finnish industrial and non-industrial area. More H$_2$SO$_4$ 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 decrease during plume ageing. NO$_x$ reduction leads to increases in [OH] and [H$_2$SO$_4$]. While the [OH] increased consistently during
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, to investigate the sensitivity of the results to the values of the value of $A$ alone is not sufficient to explain observed new particle formation. A second source of uncertainty is the sulfuric acid concentration, which was calculated using a rather simple scheme (see Sect. 2.1.1). Increases in $[\text{H}_2\text{SO}_4]$ leads to both increased $J_{\text{nuc}}$ and GR and ultimately to larger $J_{2.5}$. Results displayed in Table 3 show that $J_{2.5}$ is more consistent with observations when $[\text{H}_2\text{SO}_4]$ is increased 5 or 10-fold and when $A$ is set equal to $1 \times 10^{-6}$ like in Sihto et al. (2006). Therefore, underestimation of $[\text{H}_2\text{SO}_4]$ may explain the discrepancy between the observations and base case model results. This might be caused by underestimation of $[\text{OH}]$ or overestimation of $[\text{H}_2\text{SO}_4]$. Regarding the modelled $[\text{OH}]$ concentrations, it can be noted that they are relatively low, reaching values of around $1 \times 10^5$ cm$^{-3}$ by the end of the flights. In comparison, concentrations of around $1 \times 10^7$ cm$^{-3}$ have been reported during the daytime around noon in various atmospheric environments (Hofzumahaus et al., 2009; Petäjä et al., 2009), 0.26 $\times 10^6$ molec cm$^{-3}$ in Mace Head (Berresheim et al., 2002), and 1 $\times 10^6$–$2 \times 10^7$ molec cm$^{-3}$ in Atlanta (Kuang et al., 2008). Relatively low modelled $[\text{OH}]$ concentrations can be explained by high $[\text{NO}_x]$ concentrations which were calculated to decrease consistently from several tens of ppm down to around 200 ppb during the flights (not illustrated here). Such high concentrations of $[\text{NO}_x]$ are consistent with low $[\text{OH}]$ (see Fig. 1 in Lonsdale et al., 2012). It could thus be speculated that the model underestimates $[\text{H}_2\text{SO}_4]$ and consequently the rate of new particle formation due to overestimation of $[\text{NO}_x]$. Moreover, it should be noted that neither $\text{SO}_3$ nor low-volatile organic vapours that might have been present in the measured flue gas were not accounted for in the modelling study. Previous studies suggest that these exhaust compounds may also increase the formation rate of nucleation particles (Pirjola et al., 2015; Ehn et al., 2012; Arnold et al., 2012), which may explain the discrepancy between measurements and model calculations. Regarding the estimation of the value of $[\text{CS}]$, 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 $[\text{CS}]$ values were lower than those used as input to the model, which causes additional uncertainties.

3.5 Discussion

Each power plant (over 50 MW) in the EU has emission limits for $\text{SO}_2$, $\text{NO}_x$ 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$^{-3}$. A 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). It was observed that these low emissions can be achieved through properly
working flue-gas cleaning systems. In addition to primary emissions, flue-gas cleaning systems also seemingly affect the compounds, which can act as precursors for new particles, e.g. SO₂ tends to oxidize in the atmosphere to form SO₃ and further forms H₂SO₄, which can nucleate or condensate to particle phase. This study clearly shows 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. For example, according to Huang et al. (2014) in Xi’an and Beijing 37% of the sulfate in atmospheric particles is emitted from coal burning.

In this study the power plant plume diluted to background levels in 2 km (200–400 s), which is faster than in other in-flight measurements (Stevens et al., 2012; Junkermann et al., 2016). 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 SO₂ and CO₂ 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 enabled us to model the plume dilution on a detailed scale. From this, we were able to observe that while SO₂ and CO₂ were already diluted to background levels at a distance of 2 km – in agreement with the dilution modelling – the effect of the source on the aerosol number concentration was distinguished at distances > 2 km. We attribute this to nucleation taking place in the ageing plume.

According to the modelling results from Stevens et al. (2012), atmospheric new particle formation via nucleation of sulfuric acid begins in the flue-gas plume at 1 km distance from the coal-fired power plant, whereas the sulfuric 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 is most effective after 400 s, corresponding to a distance of approximately 2 km from the emission source in the atmosphere.

In 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. By 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 assessments.

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 between the ages of 25–55 s, the emission factor with respect to CO₂ was 2.0 × 10⁻¹⁰ (g CO₂⁻¹), as well as from ages over 400 s 8 × 10⁻¹⁰ (g CO₂⁻¹) in the FGD + FF off case. Similarly, in the FGD + FF on case, the emission factors were 4 × 10⁻⁹ (g CO₂⁻¹) (for aerosol dispersed 55–85 s in the atmosphere) and 3.74 × 10⁻¹⁰ (g CO₂⁻¹) (for aerosol dispersed more than 500 s in the atmosphere). In comparison, the primary emissions were 1.75 × 10⁻¹⁰ (g CO₂⁻¹) for FGD + FF off and 8.0 × 10⁻⁶ (g CO₂⁻¹) for FGD + FF on. Thus, new particle formation can increase the real atmospheric particle number emissions even by several orders of magnitude. It should be noted that particle formation depends strongly on the plume age [SO₂] and primary particle concentrations, and it is possible that there are some low-volatile organics or SO₃ present in the plume, affecting the nucleation.

Our observations show that the number of secondary particles formed in the flue-gas plume can be several orders of
magnitude higher than the primary particles directly emitted from the flue-gas duct. The formation can already be observed 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-plant-originating secondary particles. Such a parameterization does already exist (Stevens and Pierce, 2013), but it does not account for different types of sulfur removal technologies such as semi-dry desulfurization and wet desulfurization. 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 desulfurization. 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 compared to FGD + FF on and the total non-volatile particle number concentration was reduced by several orders of magnitude. A similar trend in primary emission reduction was detected in the atmospheric measurements. In addition, the reduction in primary emissions directly affects 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 s. This dilution timescale 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 timescale, 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 timescale, 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$_x$] were used to calculate the [OH] formation rate and further [H$_2$SO$_4$] 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$_2$SO$_4$] formation rate support the hypothesis of sulfuric acid formation, but the sulfuric acid formation itself does not totally explain the increase in the total particle number concentration. Therefore, e.g. low-volatile organics may exist on the flue-gas plume.

The sensitivity analysis of the [H$_2$SO$_4$] formation showed that the atmospheric parameterization is not enough to explain the processes in the flue-gas plume.

Comparison between the primary particles and newly formed particles 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; 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-originating secondary particles is a necessary step in understanding their importance.

The Supplement related to this article is available online at doi:10.5194/acp-16-7485-2016-supplement.

Acknowledgements. The study was conducted in the MMEA WP 4.5.2. of Cleen Ltd., funded by Tekes (the Finnish Funding Agency for Technology and Innovation). Authors would like to acknowledge Anna Kuusala and Joni Heikkilä for programming Matlab, Aleksi Malinen for measurement help. Fanni Mylläri acknowledges TUT Graduate School, KAUTE-foundation, TES-foundation for financial support. Eija Asmi and Ewan O’Connor acknowledge the support of the Nestling foundation (grant 201500326) and the Academy of Finland Finnish Center of Excellence program (project number 272041). Ville Vakkari acknowledges the financial support of the Nestling foundation (grant 201500326) and the Academy of Finland Finnish Center of Excellence program (grant 1118615). Fanni Mylläri and Topi Rönkkö acknowledge the financial support from the Academy of Finland ELTRAN (grant 293437).

Edited by: F. Khosrawi

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