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Fine and ultrafine particle number and size measurements from industrial combustion processes: Primary emissions field data

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ABSTRACT

This study is to our knowledge the first to present the results of on-line measurements of residual nanoparticle numbers downstream of the flue gas treatment systems of a wide variety of medium- and large-scale industrial installations. Where available, a semi-quantitative elemental composition of the sampled particles is carried out using a Scanning Electron Microscope coupled with an Energy Dispersive Spectrometer (SEM-EDS). The semi-quantitative elemental composition as a function of the particle size is presented. EU's Best Available Technology documents (BAT) show removal efficiencies of Electrostatic Precipitator (ESP) and bag filter dedusting systems exceeding 99% when expressed in terms of weight. Their efficiency decreases slightly for particles smaller than 1 μm but when expressed in terms of weight, still exceeds 99% for bag filters and 96% for ESP. This study reveals that in terms of particle numbers, residual nanoparticles (NP) leaving the dedusting systems dominate by several orders of magnitude. In terms of weight, all installations respect their emission limit values and the contribution of NP to weight concentrations is negligible, despite their dominance in terms of numbers. Current World Health Organisation regulations are expressed in terms of PM2.5 wt concentrations and therefore do not reflect the presence or absence of a high number of NP. This study suggests that research is needed on possible additional guidelines related to NP given their possible toxicity and high potential to easily enter the blood stream when inhaled by humans.

1. Introduction

Outdoor air pollution is a major environmental health problem affecting everyone in low, middle, and high-income countries, especially the fragile fraction of the population (especially the children, the elderly people and those people suffering from pulmonary diseases for example). According to the World Health Organisation (WHO, 2006), ambient (outdoor) air pollution in both cities and rural areas was estimated to cause 4.2 million premature deaths worldwide per year. An increasing number of epidemiological studies have made the correlation between the exposure to small particulate matter (2.5 μm or less in diameter ($PM_{2.5}$) and negative health effects such as cardiovascular and respiratory diseases and cancers. In particular, these particulate matters, referred to fine (PM with aerodynamic diameter less than 2.5 μm; $PM_{2.5}$) and ultrafine particles (also called Nanoparticles - NP) with aerodynamic diameter less than 100 nm, $PM_{0.1}$) can also vary in terms of chemical composition and structure depending on the emission source, and can, thus, have different impact on air quality and different health effects (Yang et al., 2019). The 2005 WHO Air quality guidelines (update expected in 2020), which provide guidance on

Abbreviations: PM, Particulate Matter; NP, NanoParticles; ESP, Electrostatic Precipitator; WESP, Wet Electrostatic Precipitator; PCCC, Post Combustion Carbon Capture; ELPI$^+$, Electrostatic Low Pressure Impactor; BDU, Brownian Demister Unit; WFGD, Wet Flue Gas Desulphurisation; GGH, Gas-Gas Heater; CCGT, Combined Cycle Gas Turbine; RFCC, Residue Fluid Catalytic Cracker; WI, Waste Incinerator; SCR, Selective Catalytic Reduction; CHP, Combined Heat and Power; PSD, Particle Size Distribution; TN, Total Number; SEM-EDS, Scanning Electron Microscope coupled with an Energy Dispersive Spectroscopy system

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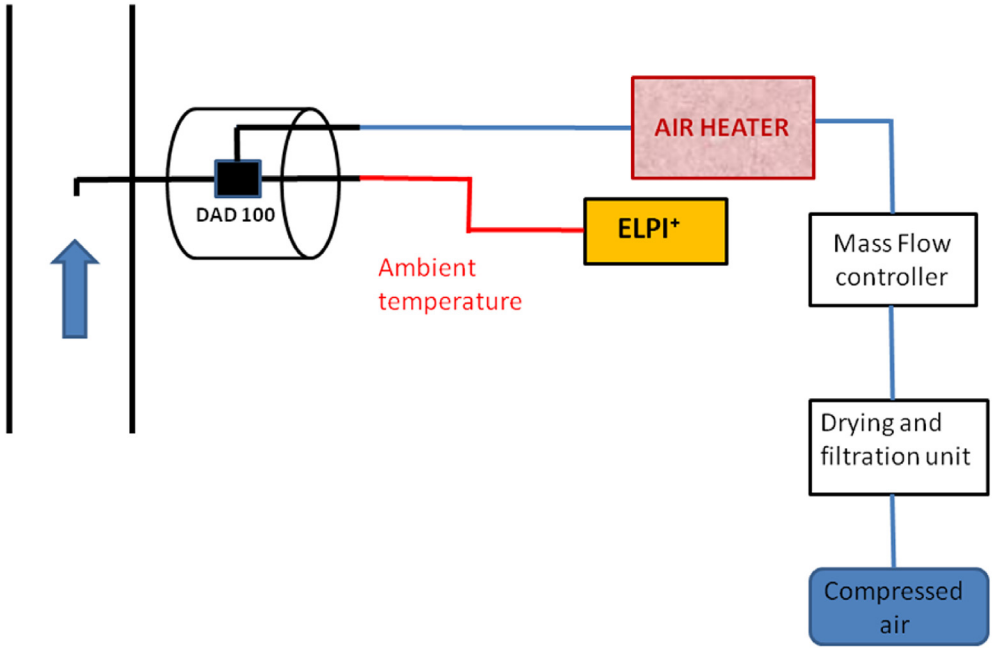

Fig. 1. Experimental layout for the dilution set-up used for the ELPI + sampling.

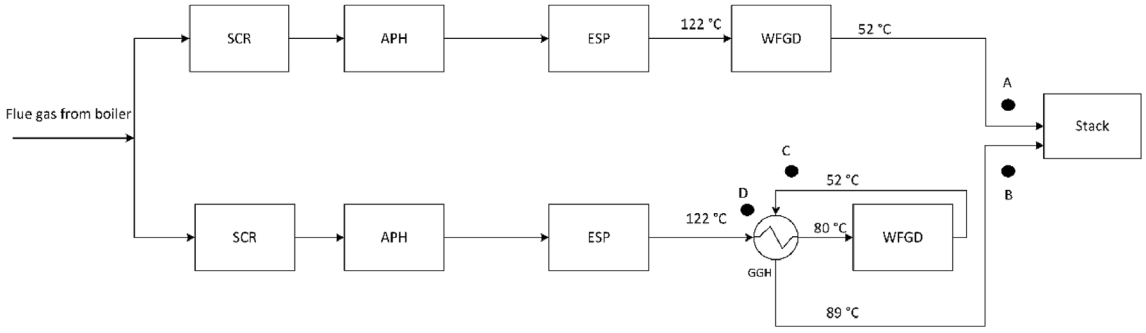

Fig. 2. Layout of the flue gas treatment system at the former ENGIE's Nijmegen power plant made-up of two parallel flue gas trains (SCR, Selective Catalytic Reduction; APH, Air Pre-Heater; ESP, ElectroStatic Precipitator; WFGD, Wet Flue Gas Desulphurisation; GGH: Gas-Gas Heater).

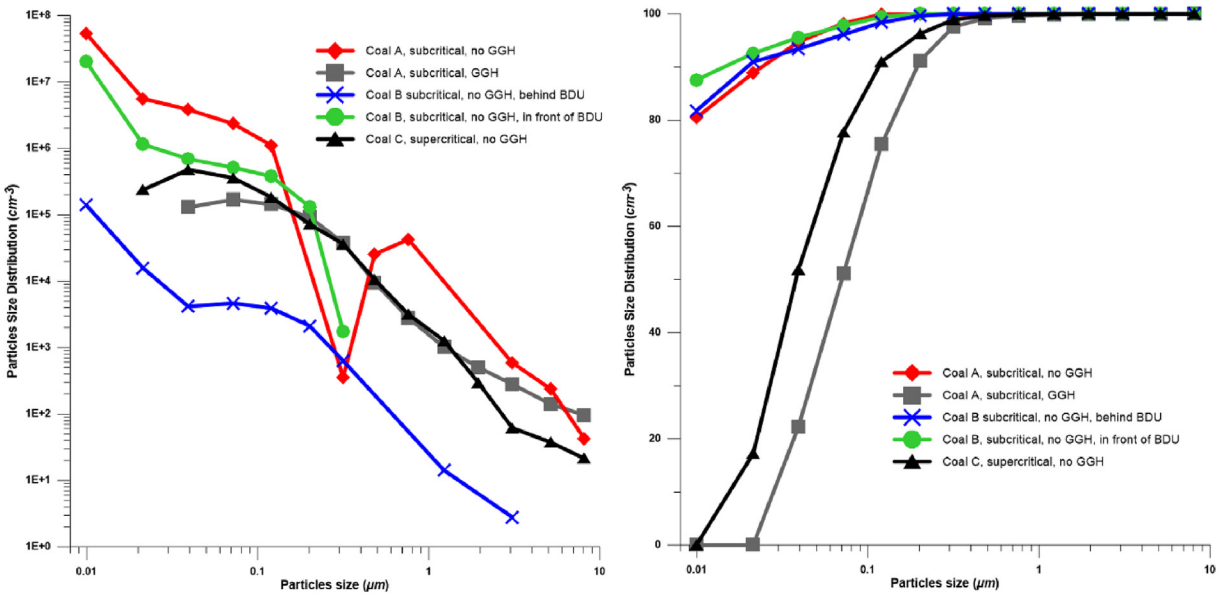

Fig. 3. Comparison of the measured particle size distributions (a) and cumulative particle size distributions (b) at all three coal fired power plants (GGH: Gas-Gas heater, BDU: Brownian Demister Unit).

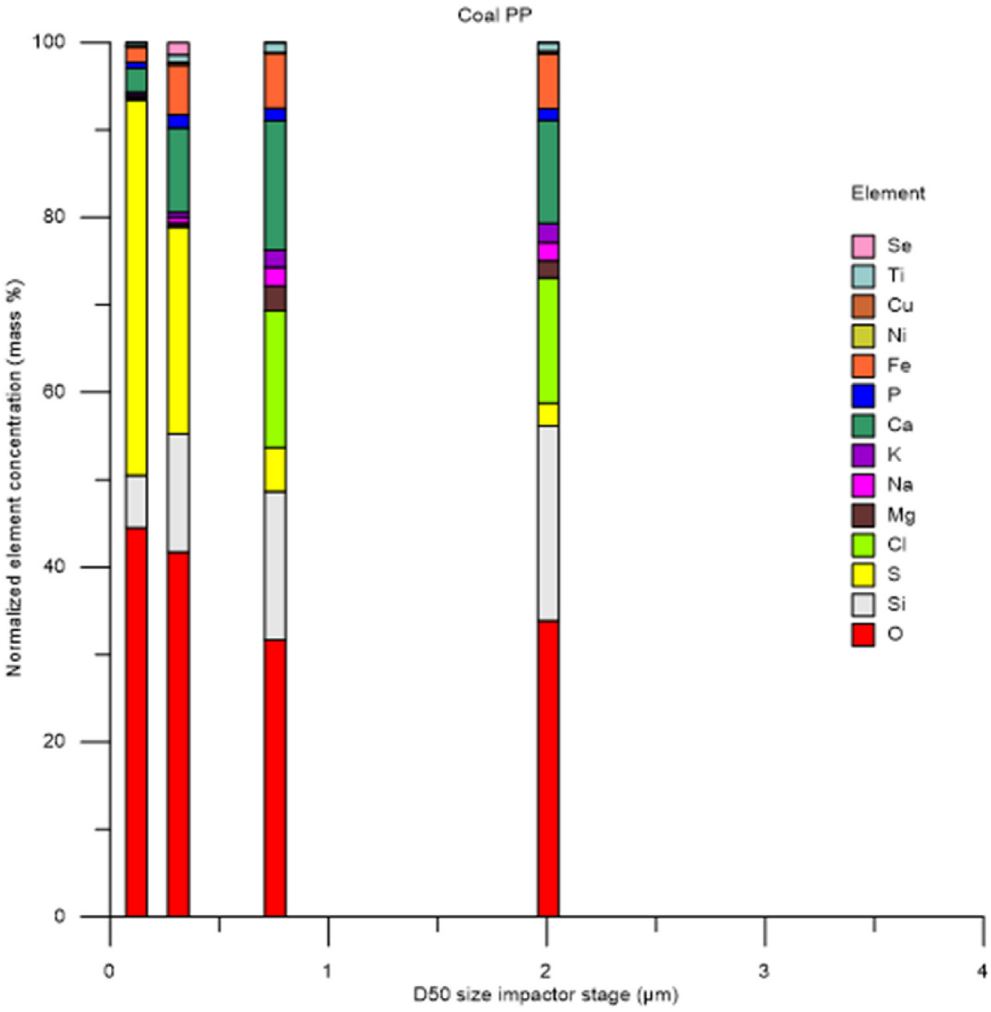

Fig. 4. Semi-quantitative elemental composition of the PM at different sizes sampled at a coal fired power plant.

thresholds and limits for key air pollutants that pose health risks, indicate that by reducing particulate matter (PM_{10}) pollution from 70 to 20 µg per cubic meter (µg m^{-3}), air pollution-related deaths could be reduced by around 15%. PM is a common proxy indicator for air pollution. It affects more people than any other pollutant. While particles with a diameter of 10 µm or less, (in weight concentration referred to as PM_{10}) can penetrate and lodge deep inside the lungs, the even more health-damaging particles are those with a diameter of 2.5 µm or less, (in weight concentration referred to as $PM_{2.5}$). These smaller particles can penetrate the lung barrier and enter the blood system. Chronic exposure to particles contributes to the risk of developing cardiovascular and respiratory diseases, as well as lung cancer (Yang et al., 2019; Lelieveld et al., 2015).

Air quality measurements are typically reported in terms of daily or annual mean concentrations of PM_{10} particles per cubic meter of air volume (m^3). Routine air quality measurements typically describe such PM concentrations in terms of micrograms per cubic meter (µg/m^3). When sufficiently sensitive measurement tools are available, concentrations of fine particles ($PM_{2.5}$ or smaller), are also reported. WHO Guideline values are therefore also expressed in these units ($PM_{2.5}$ as 10 µg/m^3 annual mean and for PM_{10} as 20 µg/m^3 annual mean).

PM consists of a complex mixture of solid and liquid particles of organic and inorganic substances suspended in the air. The major components of PM are sulfates, nitrates, ammonia, sodium chloride, organic carbon, black carbon, soot, heavy metals, mineral dust and water (WHO, 2006; Birmili and Hoffmann, 2006). Anthropogenic activities, in particular industrial combustion processes and the transport sector, are the main emission sources of these fine and ultra-fine particles. In Europe, the emission limit values from industrial processes are set by the European Directive 2010/75/EU: PM emission limit values vary widely as a function of the geographical location (continent, country and even at regional level) and type of industrial process. Two points are noteworthy. First of all, the current emission regulations are based on an overall particle mass concentration. Secondly but not less important, nanoparticles (hereafter NPs), i.e. particles smaller than 100 nm, are neither measured nor considered in these emission regulations, allegedly because of their low mass contribution. However, many published studies show that a significant portion of the particles produced during combustion processes are in the nano-size range (Fraboulet et al., 2007; Mertens et al., 2015; Mylläri et al. 2018) and as argued before, these can be very toxic due to their ability to be incorporated into the blood. Contrary to common expectations, a recent study from Trojanowski and Fthenakis (2019) revealed that modern units tend to generate a higher count of NP, though emitting less particulate mass than older units. Inversely, despite the bad reputation of municipal Waste Incinerators, several studies (Buonanno et al., 2011; Cernuschi and Giugliano, 2012) which characterized ultrafine particles emitted from these installations when equipped with bag filters highlighted a relatively low number of particles emitted at stack (between 1×10^3 and 6×10^5 part. cm^{-3}) with average diameters in the nanoparticle size range. In 2015, Buonanno and Morawska (2015) concluded the emission factors of waste incinerators are small if compared to traffic emissions.

Trojanowski and Fthenakis (2019) amongst many others therefore

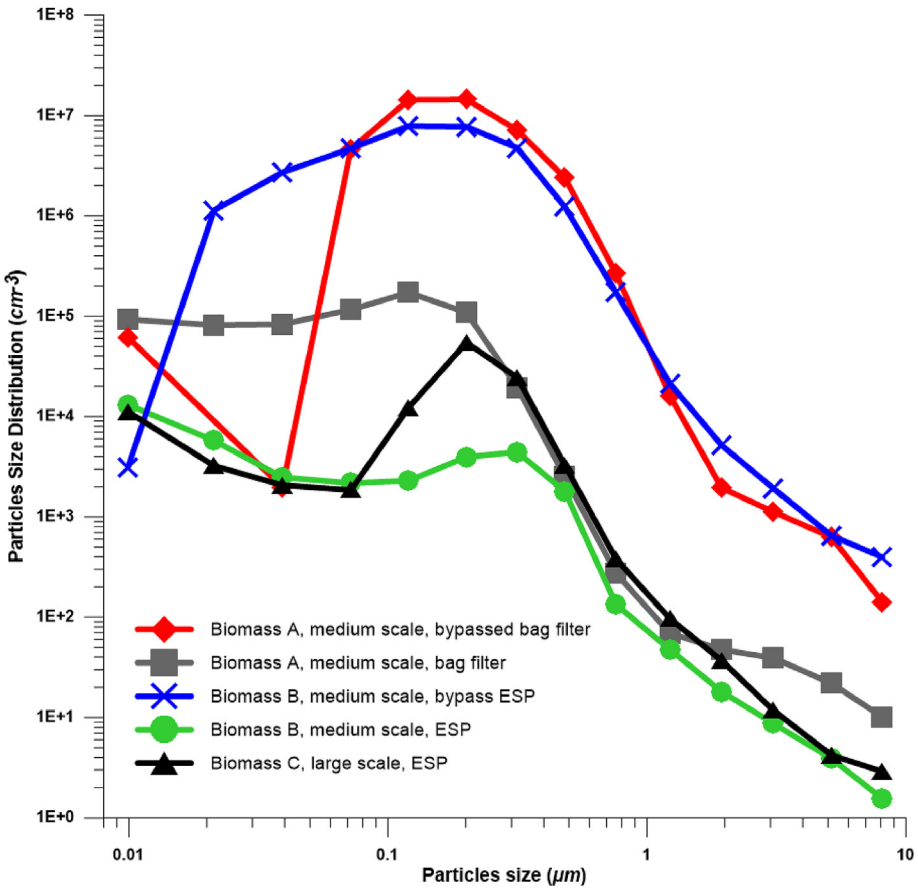

Fig. 5. Comparison of the measured particle size distributions at all three biomass fired power plants (ESP: ElectroStatic Precipitator).

support the argument of needed particle number and size regulations in addition to the current mass based emission regulations. At the time of writing this article, Belgian researchers from the University of Hasselt (Bové et al., 2019) published in Nature communications that air pollution particles which a pregnant woman inhales have the potential to travel through the lungs and breach the fetal side of the placenta, indicating that unborn babies are exposed to black carbon from motor vehicles and fuel combustion. The researchers reported in the Belgian press that today there is no legislation related to number of particles in the air and this legislation is urgently required.

This study reports and compares novel NP emission measurement data downstream of the electrostatic or fabric filters of a variety of medium- and large-scale industrial installations: coal fired power plants, Combined Cycle Gas Turbine (CCGT), Residue Fluid Catalytic Cracking installation (RFCC), Waste Incinerator (WI) and biomass power plants. The EU Best Available Technologies (BAT) documents show efficiencies of bag filters and ESP based dedusting systems higher than 99% when expressed in terms of weight concentration. Their efficiency decreases slightly for particles smaller than 1 μm but when expressed in terms of weight, still exceeds 99% for bag filters and 96% for ESP. In this study the residual NP number concentrations leaving these de-dusting systems are presented. For most of the sampled PM, semi-quantitative analysis of the elemental composition is also presented as a function of their size. The objective is to qualitatively compare the elemental composition of PM depending on the industrial source of emissions. This data set aims to support policy makers when drafting future number and size PM regulations.

2. Material and methods

This study only reports on what is sometimes referred to primary particulate matter and not secondary particulate matter. This secondary PM are gaseous when emitted from the chimney at the flue gas temperature but turn into particulates after dilution and cooling in the plume or the ambient air. Some studies show that these secondary particles can in some cases be higher than the primary PM emissions (Feng et al., 2018) but this area of research and in particular how to monitor secondary PM is still not well understood.

2.1. Measuring systems

The experimental layout presented in Fig. 1 is very similar for all emission measurement campaigns and the main measurement device used in this work is the Electrical Low Pressure Impactor (ELPI$^+$) system from Dekati.

2.1.1. Electrical low-pressure impactor (ELPI$^+$)

Upon entering the device, the particles are charged by corona charging and subsequently separated in a low-pressure cascade impactor with 14 electrically insulated collection stages. The measured current signals are proportional to the particle number concentration and size. By using kernel functions in order to account for the charging efficiency dependency on diameter and for the collection efficiencies of the different stages, the particle number concentration in every channel can be calculated. A more precise description of the original ELPI can be found in Keskinen et al. (1992) and Marjamäki et al. (2000). The ELPI$^+$ features an additional impactor stage which enlarges the measurement range covered by impactor stages from a cut-off of 30 nm down to a cut-off of 16.7 nm (Yli-Ojanperä et al. 2010). Additionally, a filter stage has been added which collects all the particles that aren't trapped in one of the impactor stages.

The charging efficiency decreases strongly with the particle size, so

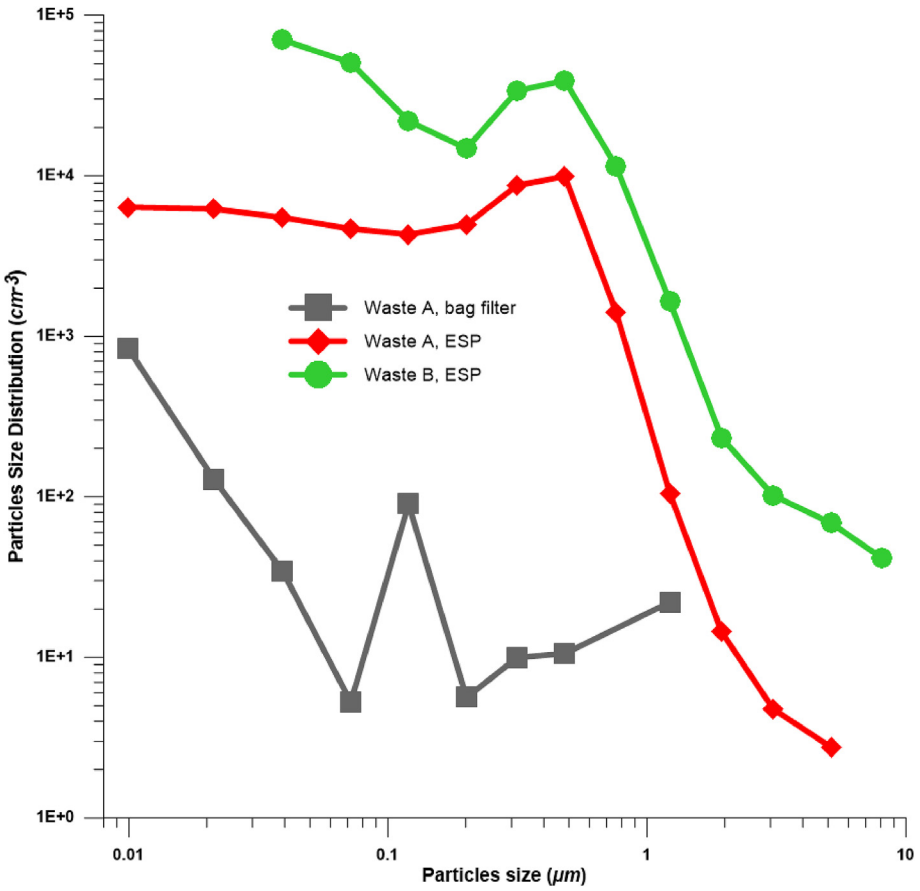

Fig. 6. Comparison of the measured particle size distributions at both waste incinerators (ESP: ElectroStatic Precipitator).

that below 6 nm no charging is expected anymore. Thereby, particles down to 6 nm can be measured. The maximum particle number concentrations that are detectable in every stage were not reached during the experiments.

2.1.2. Dilution system

When a water saturated stream is sampled (e.g. coal fired power plant with a Wet Flue Gas Desulphurisation system), water condensation must be prevented inside the ELPI$^+$ to avoid short-circuiting. In addition, in the presence of a high number of particles in the flue gas ($> 10^5$-10^6 particles), there is a risk of rapid fouling of the impactor stages. Above 1 mg of particles collected in the plate, there is a bigger risk of bouncing. Dilution of the flue gas with particle- and moisture-free instrument air and/or heating of the complete system (i.e. sampling set-up and impactor) can be used to prevent water condensation and fouling of the impactor stages. Thus, the sampling configuration as well as the impactor should be controlled at a temperature slightly above the prevailing temperature inside the flue gas duct to avoid condensation along the sampling system. This study uses the Dekati axial diluter system (DAD 100), a one-stage heated dilution system enabling as depicted in Fig. 1. Inside the heated box with the dilutor, the sampled flue gas is diluted with heated, particle- and moisture-free air. The sample box as well as sampling probe is heated to a temperature slightly above the prevailing temperature inside the flue gas duct to avoid condensation along the sampling system.

2.1.3. Particles density

When electrically-charged particles are deposited on the insulated impaction stages in the ELPI, an electrical current is generated. The algorithm established by DEKATI™, enabling to convert the current into a number of particles, is related to the particle aerodynamic diameter which is itself related to the particle density. (Charvet et al., 2015) The density depends on the chemical nature and morphology of the aerosol. In the current study, assumptions were made about the particle density depending on the type of fuel feedstock. In most cases when aqueous sulfuric acid aerosols were mainly expected, the particles were assumed to be perfectly spherical with a density of 1 g/cm^3 (close to water density). On the other hand, a particulate matter density of 2 g/cm^3 (Obaidullah et al., 2012) was adopted for emission measurements at biomass plants and waste incinerators. Based on the info from the particle composition (Lautenbach et al., 2007; Sjaak and Koppejan, 2008; Coudray et al., 2009), the mean specific density of expected compounds is closer to this value: K_2SO_4 (2.66 g/cm^3), NaCl (2.16 g/cm^3), KCl (1.98 g/cm^3), H_2SO_4 (1.84 g/cm^3), SiO_2 (2.65 g/cm^3).

2.1.4. Data quality and comparison with other devices

Sampling details at each of the locations would lead us too far from the purpose of this paper an only most important common elements with respect to the data quality are reported here. In most of the plants monitored in this study, a heated impactor was used at a temperature of 60 °C to prevent water condensation inside the system without any dilution. However, in some specific cases (i.e. high number of particles, water saturated streams after a WFGD for example), dilution of the flue gas was necessary; the lowest possible dilution factor was then chosen. Earlier research (e.g. Mertens et al., 2014, 2015) has revealed that dilution may have an effect on the measured particle size distribution. In particular, shrinking is observed in the presence of high H_2SO_4 concentrations due to the evaporation of water from the aerosols and the effect and uncertainty this has on the sampled PSD is extensively discussed in Mertens et al. (2014), 2015. Another important remark concerns the non-isokinetic sampling of the aerosols and the effect this may have on the observed aerosol sizes. This effect is only important for

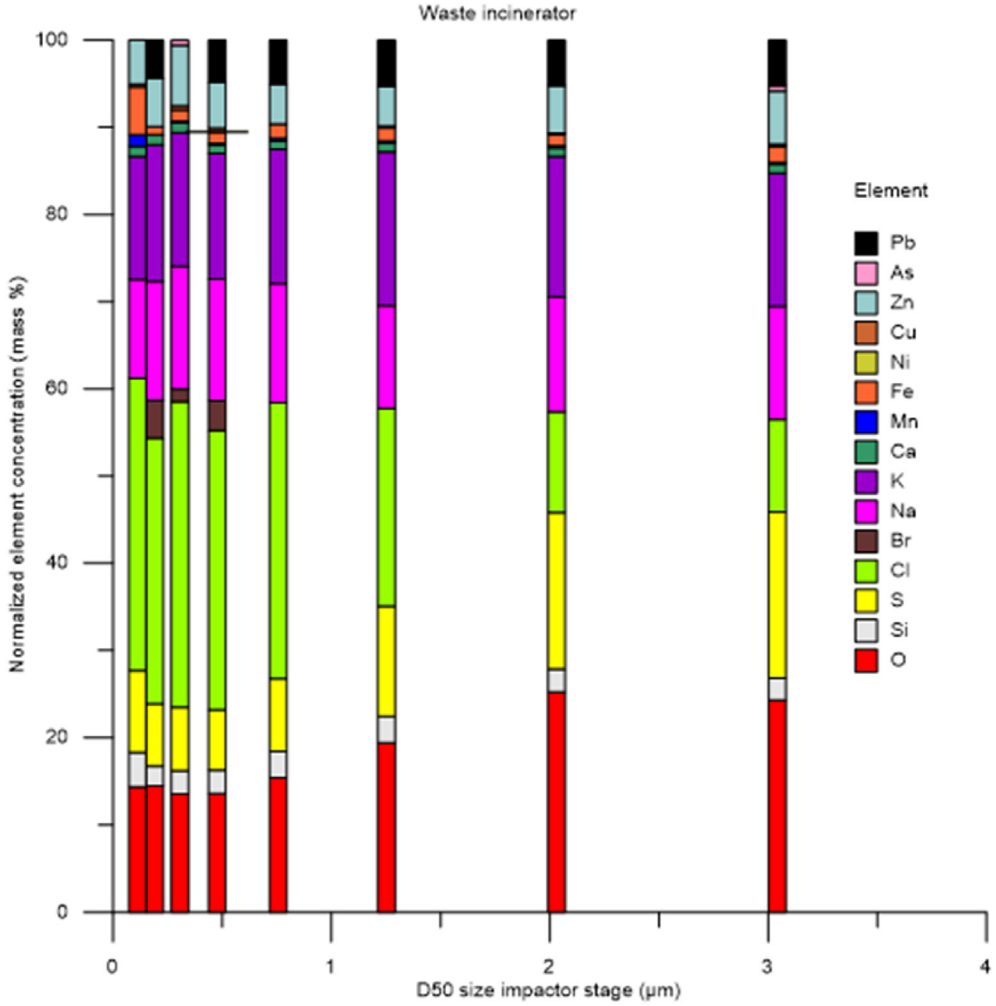

Fig. 7. Semi-quantitative elemental composition of the PM at different sizes sampled at a waste incinerator.

aerosols that are larger than a few µm (Angelo, 2008). As most of the particle sizes measured throughout this study are well below 1 µm (see below) it was judged not necessary to iso-kinetically sample the aerosols for the ELPI$^+$ measurements and thus the effect on the data negligible.

With respect to the uncertainty in particle numbers and size, we refer to our work done on comparing this exact same ELPI$^+$ set-up with a condensation particle counter (UFCPC, PALAS GmbH) for comparison on the particle number concentration, and for comparing particle size, with a modelling tool (AerCoDe) from the University of Karlsruhe (Brachert et al., 2014). This study reveals that both CPC and ELPI + correspond with AerCoDe with respect to the total number concentrations. In case of the ELPI + however, an overestimation of number concentrations (factor 2–5) was observed only for the smallest class of particle sizes (< 16 nm, filter stage). With respect to the sizes, the AerCoDe and ELPI$^+$ results match very well and show that no complete evaporation of the sulfuric acid aerosols happens even under high dilution.

The total time spent measuring at the different locations differs between locations but is in order of few days rather than hours. The sampling interval was set to 1 s and the averaging interval of the data presented in this study is usually a few hours; during which the plant ran in stable conditions.

2.2. SEM-EDS analyses

In some campaigns, the chemical composition of the particles was determined semi-quantitatively by Scanning Electron Microscopy analysis coupled with an Energy Dispersive Spectroscopy system (SEM-EDS). Jeol JSM 6400 and JSM 6400 LV instruments both equipped with an EDS system from Oxford Instrument (resolution 129 eV) were used to study both the visual aspect of a material and its elemental composition. EDS as applied for this study gives a semi-quantitative elemental composition that is not the most accurate possible, but allows to analyze small samples (< 1 mg) as is the case when sampling particles with the impactor plates of the ELPI$^+$. The deposits of accumulated particles are analyzed via window analysis where the selected area is much larger than the D50 size value of the corresponding ELPI$^+$ stage. This results in a mean composition of the corresponding size fraction. The impactor plates of the ELPI$^+$ are covered with a greased Aluminium (Al) foil to retain impacting particles. The use of these greased aluminum substrates complicates the quantification of both Al and carbon. Consequently, the concentrations of Al and C were discarded and reported concentrations are normalised to the sum of all element concentrations expressed as oxide, except Al and C.

2.3. Measurement locations

2.3.1. Coal fired power plants

Coal fired power plant A refers to ENGIE's former 600 MWe (electrical output) coal fired power plant in Nijmegen, The Netherlands. The flue gas stream is split-up into two streams (half-half) in front of the Selective Catalyst Reduction (SCR) which merge again in the stack (see Fig. 2). A unique design feature is that only one of the trains enters the

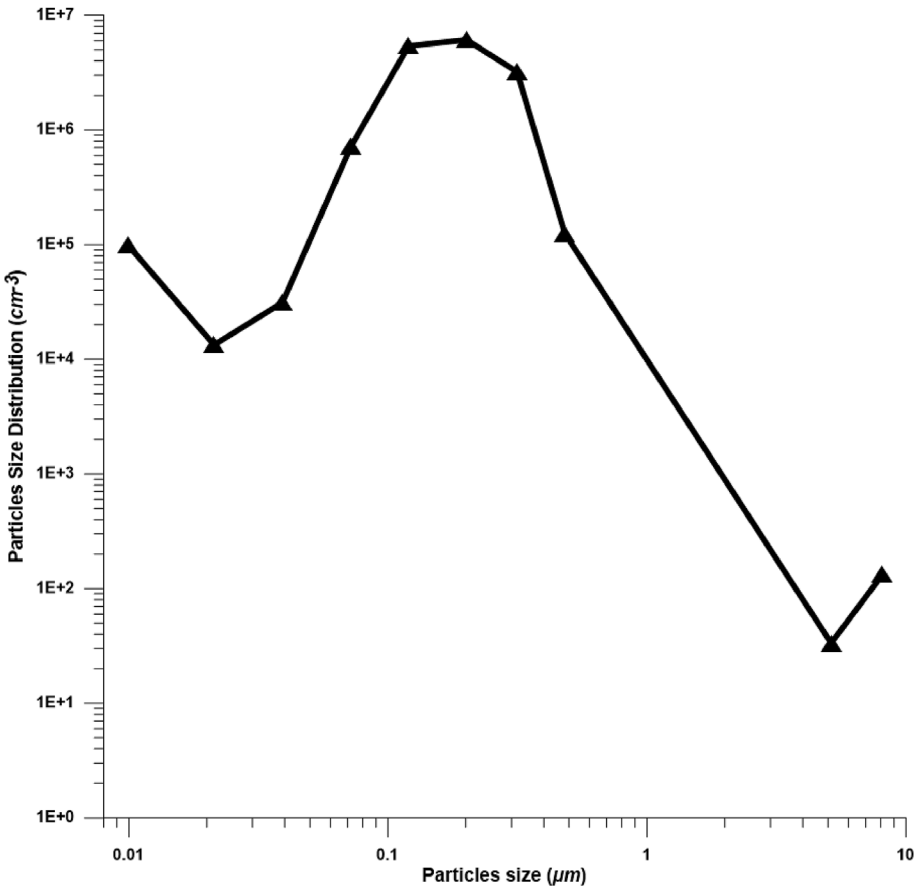

Fig. 8. Measured particle size distribution at a Residue Fluid Catalytic Cracker (RFCC).

Wet Flue Gas Desulphurisation (WFGD) right behind the ESP (Electro Static Precipitator) at a temperature of 122 °C and leaves the WFGD at around 52 °C; whilst the flue gas in the other train goes into a GGH behind the ESP where the flue gas is cooled from 122 °C to around 80 °C and then into the WFGD in which the temperature is further reduced to 52 °C. The flue gas leaving the GGH and going into the stack has a temperature of around 89 °C and is mixed with the flue gas from the other flue gas train inside the stack reheating the 'cold' flue gas to a temperature above the water dewpoint. Measurements were done downstream the WFGD at both locations: A and B as depicted on Fig. 2.

Coal fired power plant B refers to a subcritical 600 MWe coal fired power plant as well with a very similar flue gas treatment system as coal fired plant A for the case without the GGH. At this power plant, experiments were carried out on a bypass flue gas stream using a Brownian Demister Unit (BDU). The BDU (Begg Cousland, U.K.) is intended primarily for the removal of very fine mist droplets of less than 2 μm. The mechanism of operation of the BDU is combination of impingement for removing particles larger than 1–2 μm and diffusion for finer particles where Brownian motion becomes predominant. Low approach velocities are necessary in order to attain the diffusion velocities associated with Brownian movement. Finally, coal fired power plant C is a modern supercritical 1100 MWe plant with again a similar flue gas treatment system as coal fired power plant B, so no GGH installed on-site.

2.3.2. Biomass fired power plants

Biomass power plants A and B refer to two medium-scale biomass combustion plants with a total capacity of about 5 MWth. Both installations provide hot water for district heating. The boiler fired woodchips with a moisture content of about 45–50% (wet basis). The flue gas treatment of these two medium scale biomass boilers is relatively similar: downstream of the boiler, the biomass plant A is equipped with a multi-cyclone and a baghouse filter while the biomass plant B has only a baghouse filter. Both plants offer the possibility to bypass the baghouse filter. The large-scale biomass plant C refers to a reconverted thermal pulverized fuel plant firing wood pellets with a total capacity of 220 MWe at full load. Dust removal is ensured by a (dry) Electrostatic Precipitator.

2.3.3. Waste incineration plants

Emission measurements were performed at two Waste-to-Energy incineration plants (with a total capacity of respectively 110 MWe and 60 MWe). Two types of flue gas treatment systems are present at the first incinerator: particulates are either removed with bag filters (referred as Waste A, bag filter) or with an electrostatic precipitator downstream the boiler (referred as Waste A, ESP). Waste incinerator B is smaller and the flue gas treatment is very similar to WI A for the ESP case. Downstream the boiler, the flue gas is first cooled down before going into electrostatic precipitators where more than 99% of dust is removed. Flue gas is then washed by passing through aqueous caustic solutions, active carbon and electro-venturi filters to remove the residual dust and droplets.

2.3.4. RFCC

Residue Fluid Catalytic Cracking is one of the most important processes in the petroleum refinery which enables to convert catalytically heavy oil vapors into gasoline, oil and other low molecular weight paraffins and olefins. Downstream the RFCC reactor and regenerator, the flue gas goes first through the steam-generating boiler where CO is burnt as fuel to provide steam. The flue gas goes then through electrostatic precipitators to remove most of the particulate matters (1–20 μm) prior to further washing in a Wet Flue Gas Desulphurization

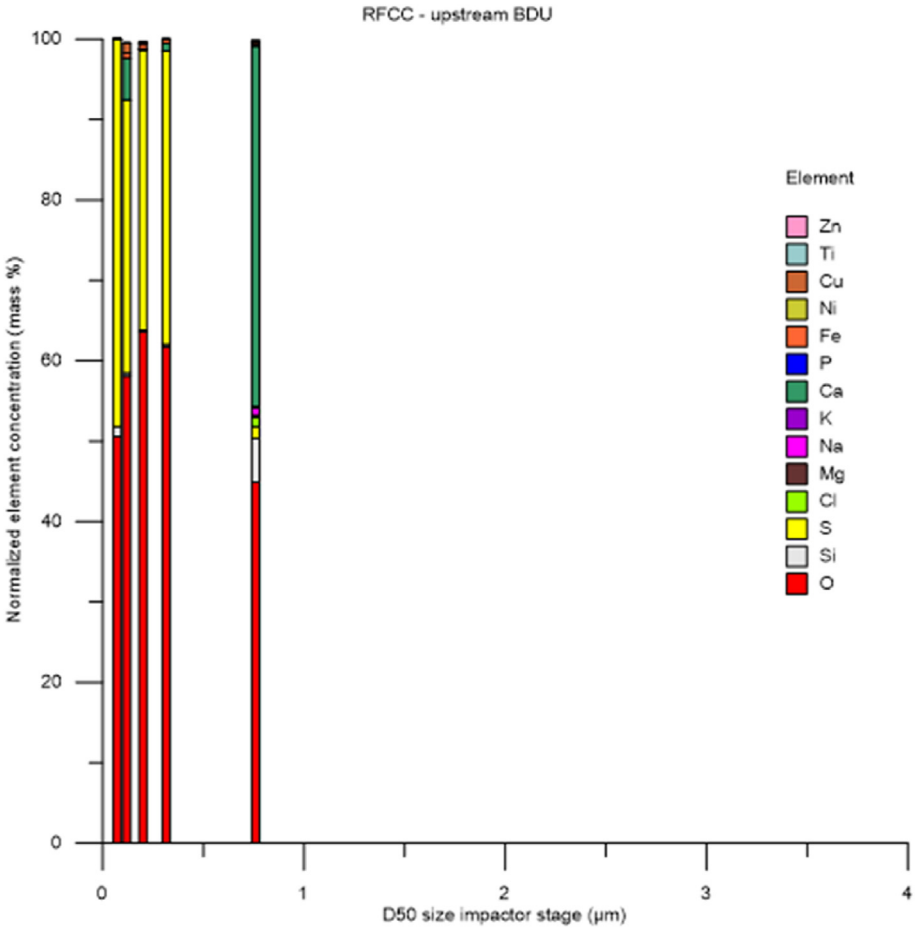

Fig. 9. Semi-quantitative elemental composition of the PM at different sizes sampled at a Residue Fluid Catalytic Cracker (RFCC).

(WFGD) unit using sea water and subsequently sent to the stack.

2.3.5. Gas-fired power plants

The combined Cycle Gas Turbine (CCGT) A refers to ENGIE's former plant in Esch-Sur-Alzette in Luxemburg which is a 380 MWe plant. CCGT B refers to a 280 MWe combined heat and power (CHP) plant. Both plants are operated in combined cycle modus which implies the operation of a gas turbine and a steam turbine. No particular flue gas treatment, apart from low NOx burners, are installed in these power plants.

3. Results and discussion

This chapter presents the results of the measurement campaigns at the different sites as a function of the fuel feedstock and the installed flue gas treatment system. Where available, the semi-quantitative elemental composition as a function of the particle size is also reported. At the end, a comparison is made between the measurements from all locations.

Needless to say that all installations do respect their respective emission limit values which depend upon the installation type, size, age and the location and vary from a few mg/Nm^3 to values exceeding 50 mg/Nm^3.

3.1. Coal fired power plants

Fig. 3a presents the number concentration measurements from the 3 coal fired power plants. In coal fired power plant A, a comparison is presented between the PM number concentrations using 2 different flue gas treatment systems: one with a Gas-Gas Heater and one without the Gas-Gas heater as described above and in detail in Mertens et al. (2015). In the absence of a GGH, the flue gas behind the ESP enters the WFGD where temperatures drop drastically and instantaneously from 122 °C to 50 °C. This creates high supersaturation conditions in which homogenous nucleation takes places converting the gaseous H_2SO_4 into aerosol H_2SO_4. This leads to high aerosol number concentrations behind the WFGD and the observed PSD is similar to reported H_2SO_4 PSD in literature (ie. 80% smaller than 0.02 µm, see Brachert et al., 2014). Leading the flue gas through a GGH therefore reduces the total PM numbers with over a factor 100: down from 6.6 E7 to 5.8 E5 which is the result of the absence of the homogenous nucleation process of sulfuric acid in the WFGD.

Fig. 3a reveals that a BDU is very efficient in removing particulate matter regardless of its size (efficiency higher than 99%, total PM numbers from to 2.3 E7 to 1.7 E5). However, the additional increase in pressure drop across the BDU would have to be provided by a flue gas blower. This would have a significant impact on the plant electricity consumption and therefore, on operating costs, especially for a full-scale plant. A BDU is therefore not seen as a feasible and sensible process to be installed on large scale industrial installations. Power plant C is a modern plant and despite a similar flue gas treatment than coal fired power plant B (absence of a GGH), succeeds in getting the PM number emissions down to only slight above coal fired power plant A when passing over the GGH (1.4 E6 against 5.8 E6). This is most likely due to lower sulfuric acid concentrations in the flue gas as well as a more efficient ESP dedusting system.

Fig. 3b shows the cumulative particle size distribution (PSD) of the PM for all cases presented above. Both the flue gas not passing through the GGH in plant A as well as the flue gas of plant B contain a very high share of very small PM (< 100 nm) which indicates the presence of

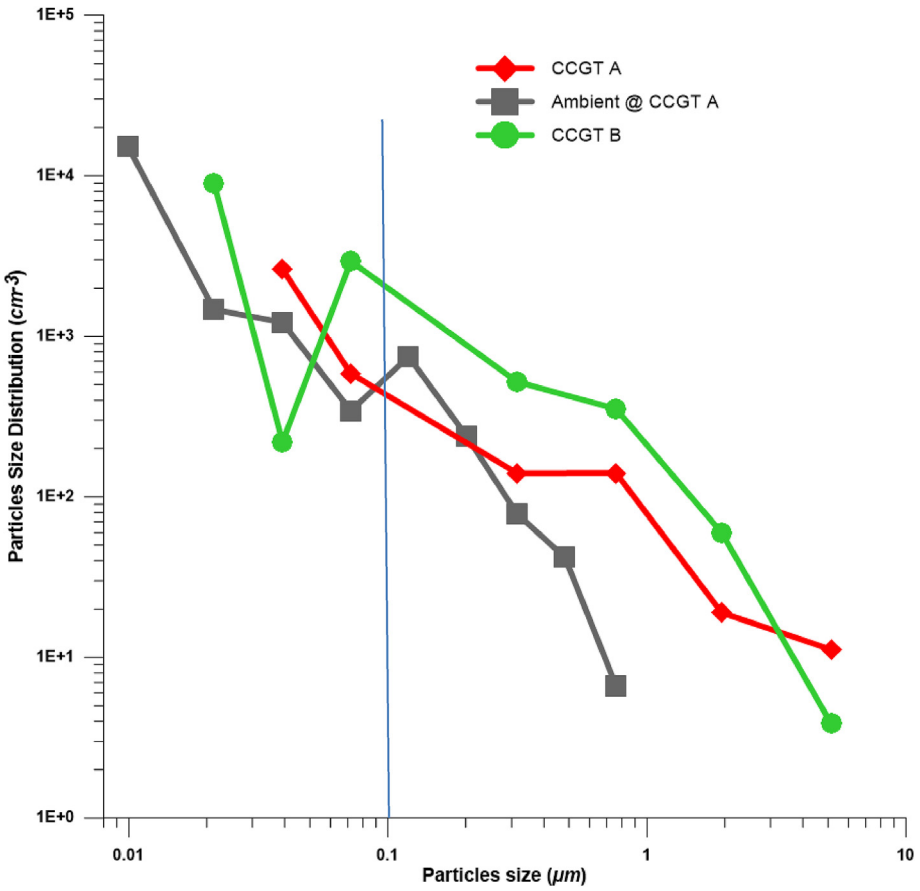

Fig. 10. Comparison of the measured particle size distributions at both Combined cycle Gas Turbines (CCGT) with the ambient air PM distribution.

H_2SO_4 aerosols. As discussed above, passing through a GGH prevents homogenous nucleation inside the WFGD resulting in fewer and relatively larger sized PM being emitted. PSD of the PM inside the flue gas of the modern power plant C reveals also larger sized PM emissions.

The semi-quantitative elemental composition of the PM (at 4 of the filter stages) as measured at the coal fired power plant C by the SEM-EDS analysis is presented in Fig. 4. The results confirm that the very fine PM (< 500 nm) are mainly S containing particles (sulfuric acid aerosols, see Brachert et al., 2014) whilst the larger PM are particles consisting of mainly Si, Ca, Cl and Fe.

3.2. Biomass fired power plants

Fig. 5 presents the number concentration measurements at the 3 biomass plants. For both medium scale biomass plants A and B, the PM number concentration is also measured when bypassing the filter. The bag filter succeeds in getting the numbers down to very low levels in both power plants, but is most efficient in power plant B. The larger scale biomass fired power plant with ESP system emits a similar amount of PM as the medium scale PP's with a bag filter. Awareness about PM emission originating from biomass combustion is increasing; in particular from small-scale wood firing. The combustion in many of these small installations is not optimised (e.g. absence of secondary combustion) and few of them are equipped with flue gas treatment systems. This results in large amounts of PM being emitted, which we can expect to be above (due to sub-optimal combustion in smaller as compared to larger units) or in the same range than what is reported here in case when the bag filter is bypassed.

No semi-quantitative elemental composition is available from these biomass plants but this topic has been studied extensively in literature. The number concentrations peak around 200 nm and this seems to be consistent for all installations. The very low numbers of NP below 50 nm suggests the absence of H_2SO_4 aerosols emitted from biomass combustion. In contrast, we can expect a high alkali content, namely Potassium (K) and Sodium (Na), together with Calcium (Ca) and some Silica (Si), the latter a consequence of soil and stone contamination. Lead and Chloride are sometimes also reported depending on the biomass composition (Nussbaumer and Lauber, 2010).

3.3. Waste incineration plants

Fig. 6 shows very low PM emissions from both WI plants: For the WI plant A, the total number of particles emitted at stack was 1.2 E^3 when the particles from the flue gas were removed with a bag filter and 5.2 E^4 with an ESP. In the second WI plant B, a total number of 2.4 E^5 particles was measured. These low concentration numbers are in agreement with previous studies performed on Waste incinerators (Buonanno et al., 2011; Cernuschi and Giugliano, 2012; Buonanno and Morawska, 2015) As one would expect, the bag filter succeeds in getting the levels well below PM numbers found in ambient air (see below). Since the chemical composition of these PM depend very much on the waste feedstock and therefore can potentially contain toxic substances, it is encouraging to see these very low PM emissions from both WI and in particular for the bag filter case, hardly anything is emitted.

Fig. 7 presents the semi-quantitative elemental composition of the particles sampled at WI in the ESP case. Waste B consist mainly of Cl salts (Na, K) and oxides of Fe, Zn, Cu and Pb. S is also present in relatively significant concentrations. Other elements are found: Mg, Ca, Br, etc. Al is discarded from the results since Al is the material for the impactor foils. Compared to coal power plants, S-containing compounds are present in lower quantities suggesting the absence of sulfates in the samples. The high proportion of chlorides and metallic

Table 1
Summary of PM numbers measured at all locations and reported per size class.

Ref.	Source of flue gas	Load	Flue gas treatment	D50 (μm)													Total Number of Particles
				0.010	0.021	0.039	0.072	0.120	0.201	0. 315	0.482	0.760	1.226	1.945	3.078	5.148	8.112	
Coal A	Power Plant - subcritical	600 MW e	GGH, wet stack	0.0 E+00	0.0 E+00	1.3 E+05	1.7 E+05	1.4 E+05	9.2 E+04	3.8 E+04	9.5 E+03	2.8 E+03	1.0 E+03	5.0 E+02	2.8 E+02	1.4 E+02	9.6 E+01	**5.9E + 05**
	Power Plant - subcritical		no GGH, wet stack	5.3 E+07	5.6 E+06	3.9 E+06	2.3 E+06	1.1 E+06	0.0 E+00	3.6 E+02	2.5 E+04	4.3 E+04	0.0 E+00	0.0 E+00	5.9 E+02	2.4 E+02	4.3 E+01	**6.6E + 07**
Coal B	Power Plant - subcritical	600 MW e	no GGH, in front of BDU	2.0 E+07	1.2 E+06	6.9 E+05	5.1 E+05	3.8 E+05	1.3 E+05	1.7 E+03	0.0 E+00	0.0 E+00	0.0 E+00	0.0 E+00	0.0 E+00	0.0 E+00	0.0 E+00	**2.3E + 07**
	Power Plant - subcritical		no GGH, behind BDU	1.4 E+05	1.6 E+04	4.2 E+03	4.7 E+03	3.9 E+03	2.1 E+03	6.3 E+02	0.0 E+00	0.0 E+00	1.4 E+01	0.0 E+00	2.8 E+00	0.0 E+00	0.0 E+00	**1.7E + 05**
Coal C	Power Plant - supercritical	1100 MW	no GGH, wet stack	0.0 E+00	2.4 E+05	4.8 E+05	3.6 E+05	1.8 E+05	7.2 E+04	3.6 E+04	1.1 E+04	3.2 E+03	1.3 E+03	3.0 E+02	6.2 E+01	3.8 E+01	2.1 E+01	**1.4E + 06**
Gas A	CCGT	380 MW		0.0 E+00	0.0 E+00	2.6 E+03	5.9 E+02	0.0 E+00	0.0 E+00	1.4 E+02	0.0 E+00	1.4 E+02	9.3E-02	1.9 E+01	0.0 E+00	1.1 E+01	9.7E-02	**3.5E + 03**
Gas B	CHP	280 MW		0.0 E+00	8.9 E+03	2.2 E+02	2.9 E+03	0.0 E+00	0.0 E+00	5.2 E+02	0.0 E+00	3.5 E+02	0.0 E+00	6.0 E+01	0.0 E+00	3.9 E+00	0.0 E+00	**1.3E + 04**
RFCC	Refinery - Residual Fluidized Catalytic Cracker			9.9 E+04	1.3 E+04	3.1 E+04	7.2 E+05	5.4 E+06	6.1 E+06	3.2 E+06	1.3 E+05	0.0 E+00	0.0 E+00	0.0 E+00	0.0 E+00	3.3 E+01	1.3 E+02	**1.6E + 07**
Biomass A	Medium Scale Combustion Plant	~5 MW	cyclone and bag filter	9.3 E+04	8.2 E+04	8.3 E+04	1.2 E+05	1.7 E+05	1.1 E+05	2.0 E+04	2.5 E+03	2.7 E+02	6.9 E+01	4.7 E+01	3.9 E+01	2.2 E+01	1.0 E+01	**6.8E + 05**
			bypass bag filter	6.1 E+04	0.0 E+00	2.0 E+03	4.6 E+06	1.4 E+07	1.4 E+07	7.2 E+06	2.4 E+06	2.7 E+05	1.6 E+04	1.9 E+03	1.1 E+03	6.3 E+02	1.4 E+02	**4.3E + 07**
Biomass B	Medium Scale Combustion Plant	~5 MW	bag filter	1.3 E+04	5.8 E+03	2.5 E+03	2.2 E+03	2.3 E+03	4.0 E+03	4.4 E+03	1.8 E+03	1.3 E+02	4.8 E+01	1.8 E+01	8.7 E+00	3.9 E+00	1.6 E+00	**3.6E + 04**
			bypass bag filter	3.1 E+03	1.1 E+06	2.7 E+06	4.7 E+06	7.9 E+06	7.7 E+06	4.8 E+06	1.2 E+06	1.7 E+05	2.1 E+04	5.2 E+03	1.9 E+03	6.5 E+02	4.0 E+02	**3.0E + 07**
Biomass C	Large Scale Combustion Plant	220 MW e		1.1 E+04	3.2 E+03	2.1 E+03	1.9 E+03	1.2 E+04	5.5 E+04	2.5 E+04	3.3 E+03	3.8 E+02	9.7 E+01	3.7 E+01	1.2 E+01	4.2 E+00	2.9 E+00	**1.1E + 05**
Waste A	Waste incineration plant		bag filter	8.4 E+02	1.3 E+02	3.5 E+01	5.3 E+00	9.0 E+01	5.6 E+00	1.0 E+01	1.1 E+01	0.0 E+00	2.2 E+01	0.0 E+00	0.0 E+00	0.0 E+00	0.0 E+00	**1.1E + 03**
Waste A	Waste incineration plant		ESP	6.4 E+03	6.2 E+03	5.5 E+03	4.7 E+03	4.3 E+03	5.0 E+03	8.7 E+03	9.9 E+03	1.4 E+03	1.1 E+02	1.4 E+01	4.8 E+00	2.8 E+00	0.0 E+00	**5.2E404**
Waste C	Waste incineration plant		ESP	0.0 E+00	0.0 E+00	7.0 E+04	5.1 E+04	2.2 E+04	1.5 E+04	3.4 E+04	3.9 E+04	1.2 E+04	1.7 E+03	2.3 E+02	1.0 E+02	6.9 E+01	4.1 E+01	**2.4E + 05**
Ambient 1	Ambient air (@CCGT)			1.5 E+04	1.5 E+03	1.2 E+03	3.4 E+02	7.5 E+02	2.4 E+02	7.8 E+01	4.2 E+01	6.6 E+00	6.8E-01	9.7E-01	3.6E-01	2.1E-02	2.8E-01	**1.9E + 0–4**
Ambient 2	Ambient air (@waste incinerator c)			1.6 E+04	6.3 E+03	3.3 E+03	1.7 E+03	8.3 E+02	2.3 E+02	3.3 E+01	0.0 E+00	9.9 E+00	7.6 E+00	2.9 E+00	0.0 E+00	1.5 E+00	0.0 E+00	**2.8E + 04**

species is consistent with previous studies, with the potential release of chlorine from the plastic fraction of the waste feed (Cernuschi and Giugliano, 2012).

3.4. Residue Fluid Catalytic Cracker

Fig. 8 presents the measured PM concentrations emitted from the RFCC plant. A high number concentration is emitted from the plant with most of the PM between 0.1 and 0.5 µm. Fig. 9 shows the PM size fractions smaller than 0.5 µm are dominated by S and O, suggesting H_2SO_4 aerosols. The tested size fraction above 0.5 µm consists mainly of Ca and O so we may wonder whether there is some carry-over of gypsum out of the WFGD system into the flue gas. No comparison is available from other RFCC installations so future work is needed to better understand PM emissions from RFCC installations.

3.5. Gas-fired power plants

Emissions from both plants are very low and comparable or even lower than the number of PM present in the ambient air (Fig. 10). The combustion air for these large scale CCGT plants is filtered before being sucked into the combustion chamber whilst during combustion, we do not expect large amounts of PM being formed which could explain a lower concentration in the flue gas of the gas turbines as compared to the inlet/ambient air. As explained in the introduction, our measurement set-up is not suited for measuring secondary particles and since CCTG flue gases contain NO_x, a precursor for secondary PM formation, we cannot simply conclude that CCGT's clean up the ambient air as some people claim. No information is available on the semi-quantitative elemental composition of the PM inside the flue gases since it would take an enormous time to sample sufficient material on the ELPI$^+$ stages permitting a SEM-EDS analysis.

3.6. Overview of all measurements

Table 1 serves as a summary for all measurement locations and the PM numbers are reported per size class. Highest total PM concentrations are emitted from the coal fired plants and the RFFC plant. This is mainly due to the high level of sulfuric acid aerosols which are usually formed inside WFGD systems when going through the dew point of sulfuric acid in the presence of supersaturation conditions (fast wet cooling). For biomass plants and waste incinerators, emitted primary PM number levels are low, and even non-significant for the CCGT power plants.

4. Conclusions

This study is to our knowledge the first to present the results of online measurements of residual nanoparticle numbers downstream of the flue gas treatment systems of a wide variety of medium- and large-scale industrial installations. It must be stressed that only primary emissions are reported in this study and it is likely that secondary particle formation will be substantial for flue gases rich in NOx, SOx (both from combustion) and NH_3 (eg. from a SCR Denox system) once they cool down. In fact, depending on these pollutant concentrations in the flue gas and the atmospheric conditions, secondary PM concentrations can exceed the primary concentrations (Feng et al., 2018).

Although all dedusting techniques prove to be very efficient, residual NP concentrations emitted from the coal fired plants and the RFFC plant were found to be high, mainly due to the high level of sulfuric acid aerosols. For biomass plants and waste incinerators, emitted NP number levels are low but as the bypass measurements reveal, it is crucial to ensure a continuous well-functioning of the flue gas treatment system. Primary PM concentrations emitted from large scale gas turbines are lower than PM levels in ambient air due to the filtering of the air inlet.

EU's Best Available Technology documents (BAT) show removal efficiencies of Electrostatic Precipitator (ESP) and bag filter dedusting systems exceeding 99% when expressed in terms of weight. Their efficiency decreases slightly for particles smaller than 1 µm but when expressed in terms of weight, still exceed 99% for bag filters and 96% for ESP. This study reveals that in terms of particle numbers, residual nanoparticles (NP) downstream of the dedusting systems are dominant in the total number of residual PM exceeding the larger residual PM by several orders of magnitude. In terms of weight, all installations respect their emission limit values and the contribution of NP to weight concentrations is negligible, despite their dominance in terms of numbers. Current World Health Organisation regulations are expressed in terms of PM2.5 wt concentrations and therefore do not reflect the presence or absence of a high number of NP. This study suggests that research is needed on possible practical ways to measure such emissions, and on additional guidelines related to NP given their possible toxicity and high potential to easily enter the blood stream when inhaled by humans.

Authors contribution

Jan Mertens: conceptualization, methodology, investigation, data curation, writing original draft and review. H. Lepaumier: investigation, writing original draft and review. P. Rogiers: investigation, writing original draft and review. D. Desagher: investigation, data curation. L. Goossens: Writing - Review & Editing,. A. Duterque: Writing - Review & Editing. E. Le Cadre: Writing - Review & Editing. M. Zarea: Writing - Review & Editing. J. Blondeau: data curation, writing original draft and review. M. Webber: supervision.

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