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Emissions of ultrafine and nanoparticles from WTE (waste to energy) plants

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EXECUTIVE SUMMARY (500-550 WORDS)

Most recent air quality issues related to particulate matter pollution are addressed towards fine (FP) and ultrafine (UFP) size fractions, namely those particles with dimensions included in the range from 2.5 μm down to the minimum practical detection limit of few nm, with the smallest fractions most significantly involved in health related issues. Attention has been recently dedicated to their origin and generation from combustion sources: however, the large majority of investigations are dedicated to vehicle emissions, with rather limited studies available in the general field of stationary combustion and even less informations for the waste to energy sector.
Present paper reports on the experimental evaluation of UFP and nanoparticle size fractions emitted from full scale incineration plants. The investigation involved three different urban waste to energy plants, equipped with flue gas treatment configurations included in most recent BAT reference options. The measurements were conducted with a dedicated sampling instrumentation, specifically developed and assembled for evaluating UFP and NP size fractions (particles less than 0.1 μm and 0.05 μm aerodynamic diameter, respectively), either of primary than of condensible origin: this latter, arising from semivolatile flue gas components nucleation and/or condensation phenomena driven by atmospheric dispersion, dilution and cooling, might significantly increase the primary UFP concentrations and alter their size distribution. Particle number concentrations and size distributions were measured with an electrical low pressure impactor (ELPI™), giving values for 12 different size intervals in the range 7 nm - 10 μm.
Mean number concentrations of UFP resulting from cold sampling tests are included between 4000 and 70˙000 particles cm^{-3}**,** with the ultrafine fraction largely prevailing in size distributions and with mode diameters consistently located in the nanoparticle range. Hot sampling results in lower levels with respect to the corresponding dilution values, with particle fractions of condensible origin thus confirming their effect on increasing the emitted concentrations. Results as a whole address further some differences arising from the flue gas treatment process design, with the utilization of wet scrubbing that seems to enhance the presence of primary UFP as well as their formation from condensable origin. Finally, even the higher stack gas concentrations detected exceed only slightly combustion air measured values, included between 14˙000 and 32˙000 particles cm^{-3}.

INTRODUCTION

It is widely known that particulate matter emitted from combustion processes varies greatly in size and composition (Lighty et al., 2000). Whereas a general agreement about the definition of the ultrafine fraction (UFP) has still to be reached, the atmospheric sciences community currently adopts the term for indicating the size fraction of particles under 0.1 μm. UFP particles are mainly constituted by carbonaceous agglomerates and of some of the inorganic components of the fuels.

Although main concerns of UFP were originally related to the potential new class of environmental hazards arising from the development of nanotechnologies, with most of the research studies oriented to indoor exposure in the industrial sector, attention has been recently also addressed to their emissions from combustion activities (Biswas and Wu, 2005): however, the large majority of investigations are dedicated to traffic emissions (e.g., diesel vehicles) (Kittelson, 1998), with rather limited studies for stationary combustion sources (Christensen et al., 1996; Gomez-Moreno et al., 2003; Nielsen et al., 1996; Yi et al., 2006; Maguhn et al., 2003; Buonanno et al., 2008). Further limitations in this latter field arise from the approaches adopted for measurements, generally conducted with conventional hot stack gas sampling, with no informations thus available on the potential effects on UFP number concentrations of particle nucleation and/or condensation phenomena, arising from semivolatile flue gas components and driven by atmospheric dilution (Wehner et al., 2002).
The research project "ULTRAPART", conducted by Politecnico di Milano and Laboratory for Energy and Environment (LEAP) in Piacenza, was recently established within this latter field of interest, with the main task of evaluating UF and NP emissions from stationary combustion and industrial activities. The paper outlines its main scientific contents, with particular reference to the most relevant aspects of the measurement approach adopted, and report the results obtained from the investigations conducted on different plants in the waste to energy (WTE) sector.

MATERIALS AND METHODS

The investigation involved three different WTE plants, all included within the BAT (Best Available Techniques) reference options for WTE sector (EC, 2006) and whose main design characteristics are reported in Table 1. The plants, with a total throughput between 600 and 1200 ton/day of urban waste, are equipped with moving grate furnace and secondary air injection for combustion and a waste heat boiler for CHP (combined heat and power) production through a steam turbine. Flue gas treatment configurations include different process designs, based on dry (plant 1 and 2) or combined dry/wet (plant 3) technologies for particulates, acid gases and trace pollutants removal and on SCR (Selective Catalytic Reduction) units for NO_x removal and simultaneous trace organics conversion, operating in tail-end position at 180°C for plant 1 and 250°C for plant 3 and in a high-dust position at 250°C in plant 2.

Table 1 - Process design configuration of WTE Italian plants utilised in the comparative evaluation of PCDD/F total release.

Plant ID	Capacity (tpd)	APCD(*)
1	900 - 1200	ESP+DA (soda ash + AC) + FF + SCR (tail end, 180°C)
2	650 - 1200	SCR (high dust, 250°C), DA (lime + AC), FF
3	600 - 700	Quencher + DA (Sorbalit™ + AC) + FF + WS (water + NaOH solution) + SCR (tail end, 250°C)

(*) APCD - Air Pollution Control Devices: SCR: selective catalytic reduction, ESP: electrostatic precipitation, DA: dry absorption system, WS: wet absorption system, FF: fabric filter, AC: activated carbon.

The sampling assembly utilized was specifically designed for the evaluation of both primary and condensible UFP fractions through dilution techniques of sampled flue gas. Stack gas dilution is applied for simulating the behavior of the emissions under atmospheric dispersion, dilution and cooling conditions (England et al., 2007; Corio et al., 2000). The effects of dilution depend basically on the primary particulate matter concentration and the semivolatile compounds content of the emissions (Chang et al., 2004; Leskinen et al., 2007). Dilution can trigger new particle formation (Russell et al., 2009) by nucleation (homogeneous condensation) of condensable gases in two ways: by cooling the gas, decreasing thus the vapor pressure of the semivolatile species which then tend to condensate, and by decreasing the primary particulate matter concentration in the emissions which otherwise would serve as a surface for heterogeneous condensation processes, thus reducing the possibility of nucleation. Nucleation thus increases the particle number concentration while it has almost no observable effect on mass concentration, with the size distribution peaking in

the smallest diameters. On the other hand, heterogeneous condensation may increase the mass concentration and shifts the particle diameters towards larger values: the number concentration might thus decrease as the particles with the smaller diameters grow (condensational growth) or coagulate with each others. Although the actual dispersion in the atmosphere will be stronger than the effect created with the dilution ratios applicable with the sampling device, the sampling assembly might give an insight of the behavior of the particles immediately after stack emission.
The line, illustrated in Figure 1, includes a dilution system, designed in accordance with EPA CTM-039 (US EPA, 2004), integrated with the particulate matter measurement device. Sampling is performed through an isokinetic probe, in series with two cyclones for removal of ultracoarse (> 10 µm) and coarse (> 2.5 µm) particles, respectively, and operated in conventional hot conditions. Dilution is conducted downstream with a mixing cone, which provides controlled dilution ratios (DR) for the flue gas stream with HEPA filtered and conditioned air prior to a residence chamber, whose outlet section is connected to the particle counting device. Real time measurements of number concentrations and size distributions (1 sec interval) are obtained with an electrical low pressure impactor (ELPI™ - Dekati Ltd., Finland), capable of measuring simultaneously number concentrations and particle size distributions in the size range 0.007-10 µm with 12 channels and a final filter stage. The impactor is equipped with an external heating system to regulate the instrument's temperature during hot sampling without dilution.
All samplings were conducted with WTE plants in continuous operating regime at design conditions, with measurements campaigns including stack hot and cold dilution sampling at three different DR ranges and background combustion air sampling.

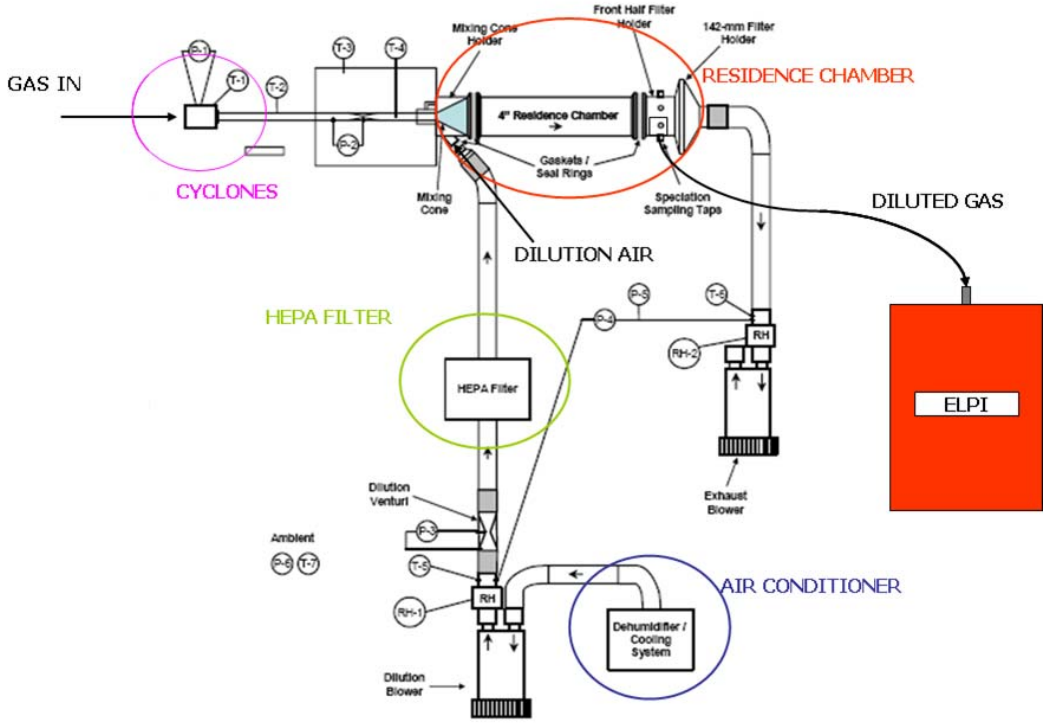

Figure 1 - Sampling and measurement line utilized in the experimental investigation.

RESULTS AND DISCUSSION

Concentration levels and mean particle size distributions obtained during the different sampling conditions utilized for every plant investigated are reported in Figures 2-7. For all test conditions available, number concentrations are plotted in terms of the main statistics of interest derived from 1 sec data measurement, including mean, median, interquartile range (25th - 75th percentile), minimum and maximum values.

For plant 1, mean concentration levels around 2800 particles/cm^3 were obtained during hot sampling, with a sharp increase in dilution tests to values in the range 10˙500 - 17˙000 particles /cm^3 (Figure 2), thus confirming the expected effects arising from flue gas dilution and cooling on particles formation of condensible origin. Number concentrations measured with dilution are not particularly affected by dilution ratios, with almost constant mean levels around 10˙500 particles/cm^3 at low (DR = 15-20) to medium (DR=25-35) dilutions and a slight increase to 17˙000 particles/cm^3 for the highest range of DR applied (DR = 40-55), corresponding to an increase, with respect to hot tests, included between 4 and 6 in terms of mean concentration ratios. Despite this dilution effects in enhancing concentrations, stack flue gas values result constantly lower than corresponding levels measured in background combustion air, where nearly 32˙000 particles/cm^3 were detected. Particle size fractions are clearly dominated by NP, representing roughly 86% of total number concentrations for hot sampling and increasing to almost 93% for high dilution sampling, thus confirming formations from condensible origin already claimed for concentration levels: further agreement is observed also from size distributions results, generally unimodal (Figure 3) and with the mode constantly detected in the last impactor stages, corresponding to the nanoparticles interval.

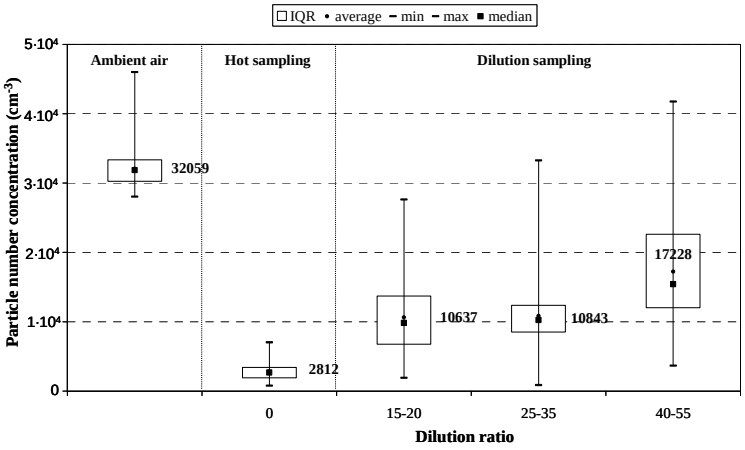

Figure 2 - Particle concentration levels - plant 1.

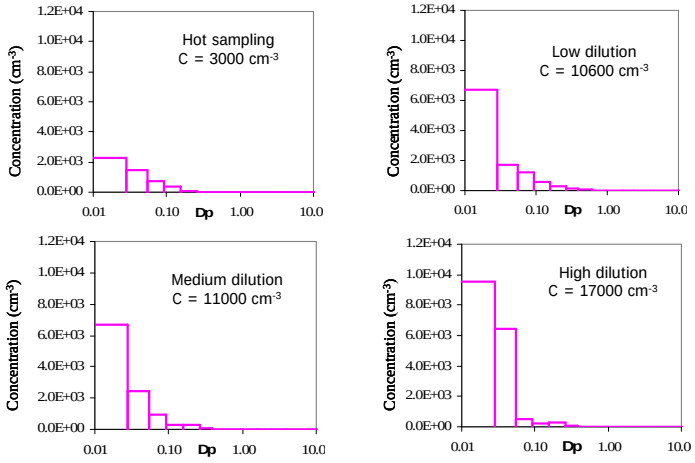

Figure 3 - Particle size distributions - plant 1.

Measurements conducted on plant 2 give general results consistent with plant 1 investigation, although with slightly lower concentration levels. Mean particle concentrations obtained (Figure 4) are essentially constant at 4000 particles/cm^3 for low to medium dilutions, with a slight increase to 7˙000 particles/cm^3 for the highest dilution but still significantly lower than background air measured levels of 13˙500 particles/cm^3. Likewise, size fractions result mainly characterized by the presence of NP, included between 71% at low dilutions and increasing to almost 82% at the highest

DR range, with corresponding unimodal particle distributions and mode diameters located in the nanoparticle size range (Figure 5).

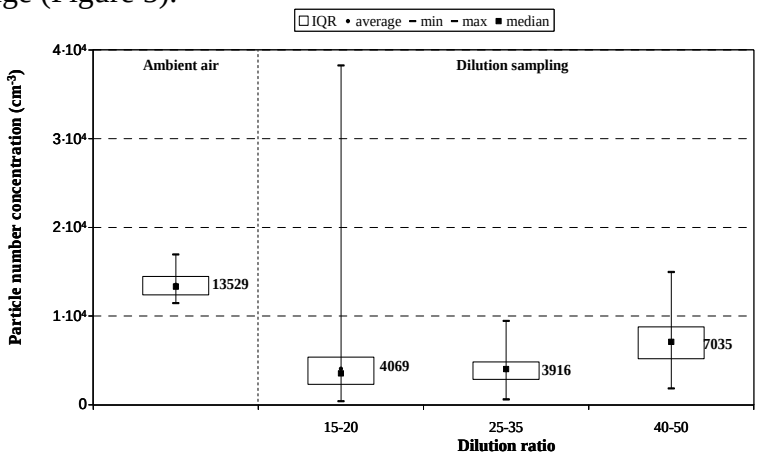

Figure 4 - Particle concentration levels - plant 2.

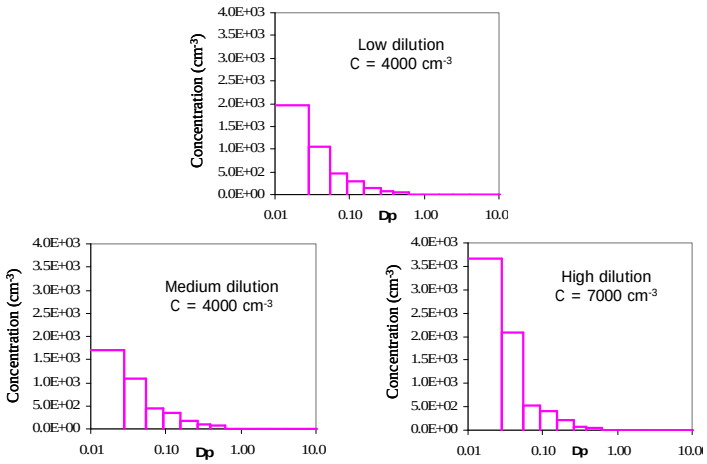

Figure 5 - Particle size distributions - plant 2.

With respect to the other WTE investigated, monitoring campaigns at plant 3 give concentration levels slightly higher and somewhat more regularly dependent on dilution ratios. Hot sampling values around 25˙000 particles/cm^3 are still lower than dilution measurements, showing a progressive increase from nearly 41500 particles/cm^3 for low dilutions (DR = 15-20) to almost 50˙000 particles/cm^3 at medium dilutions (DR = 25-35) and to roughly 70˙000 particles/cm^3 for the higher dilutions (DR = 40-50): with respect to hot tests, dilution thus drives an increase in concentrations between 2 to 3, confirming particles formation from condensible origin. Stack concentrations increase is also measured with respect to combustion air, characterized by particle levels around 20˙000 particles/cm^3 and thus comparable with those detected for the other plants where, however, this increase was far from observed. Despite the theoretical complexity of all the chemical and physical mechanisms involved in condensible UFP formation, the wet scrubbing processes utilized in plant 3 might be claimed as a design configuration factor capable of influencing the observed differences, through the enhancement of nucleation effects of residual species arising from the increase in flue gas absolute humidity. Recent experimental data available in this particular field of interest, both for wet flue gas cleaning in stationary combustion (Sinanis et al., 2008) and for diesel engine emissions (Ninga et al., 2004; Morawska et al., 2008) as well as for atmospheric studies (Biskos et al., 2009; Russell et al., 2009), address the potential of chemical reaction pathways involving oxidized sulphur compounds and water vapour in enhancing UFP nucleation processes. Size fractions obtained, still very similar to those resulting from the other plants investigated, are always characterized by the prevailing presence of nanoparticles, representing from 78% in hot sampling to nearly 88% for the highest DR range and with a smooth progressive increase with dilution, in accordance to the corresponding variations observed in

concentrations and attributable to newly formed particles from condensible origin. Same considerations apply essentially to size distributions (Figure 7), clearly unimodal for all sampling conditions and with mode diameters located, as usual, in the NP range.

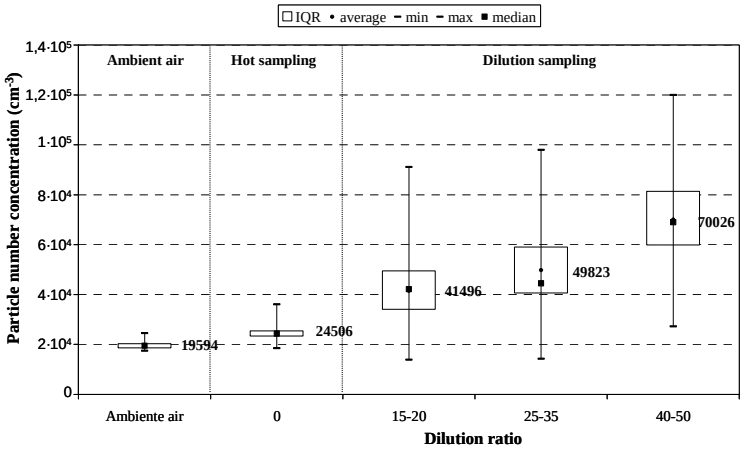

Figure 6 - Particle concentration levels - plant 3.

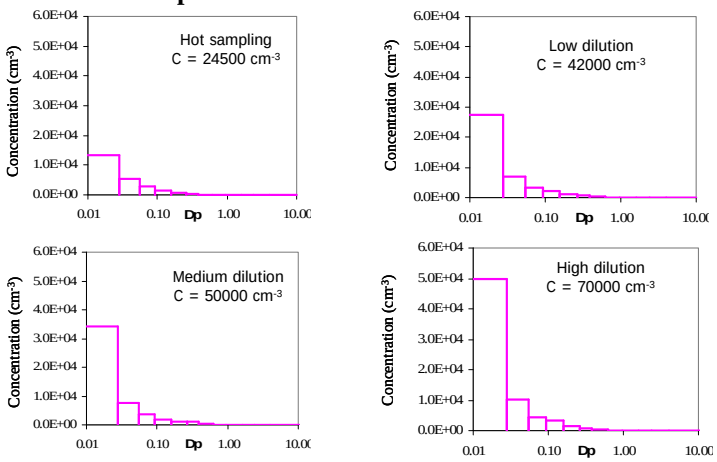

Figure 7 - Particle size distributions - plant 3.

CONCLUSIONS

Extensive measurements of UF and NP emissions from WTE plants, still poorly addressed in the specific field of interest, were conducted with a dedicated sampling assembly, especially designed for the evaluation of primary as well as secondary fractions of condensible origin. Experimental investigations on three different plants, designed in accordance with BAT reference options for combustion and flue gas treatment technologies, confirm the effect of dilution driven new particles fraction of condensible origin on the emitted concentrations, with a progressive increase of measured levels with increasing dilution ratios and with the higher levels generally detected for the highest dilution ratios applied during sampling. For all sampling conditions, UFP fractions largely prevail in number particle size distributions, with mode diameters located in the nanoparticle size range: in accordance with the dilution effects observed for concentrations, cold sampling measurements further result in a general, although sometimes rather smooth, increase of the smallest nanoparticle fractions. Results as a whole further point out potential differences arising from the flue gas treatment process design, with the utilization of wet scrubbing that seems to enhance, through the corresponding increase in flue gas water vapour content, the presence of primary UFP as well as their formation from condensable origin. Finally, despite the measured increase in emission levels during dilution sampling, even the higher stack gas concentrations detected exceed only slightly background combustion air values.

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