Laboratorio Energia e Ambiente Piacenza
(Energy and Environment Laboratory Piacenza)

A Consortium participated by Milan Polytechnic

Emissions of Fine and Ultrafine Particles from stationary combustion plants

Final Summary

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1 INTRODUCTION

This document summarizes the results of a study which was carried out by LEAP laboratory (Energy and Environment Laboratory Piacenza), a consortium supported by Politecnico di Milano. The study was commissioned by Federambiente, and deals with the issue of *Emissions of fine and ultrafine particles from stationary combustion plants*.

The study was dedicated to the assessment of the general framework of available scientific Knowledge and to the critic evaluation of the formation and production phenomena, the extent of source emissions and the potential implications of fine and ultrafine particulates from combustion plants for the entire size spectrum of emitted particles, from the minimum detectable dimension of a few nanometers (1 nanometer = 1 millionth of a millimeter) up to the limit of 10 microns (1 micron = 1 thousandth of a millimeter), beyond which the particles, being coarser and easily settleable, are largely retained by the upper airways, thus loosing most of their potential significance for health impacts.

Ultrafine particulates and nanoparticles, the focus of this study, cannot be measured with the equipment normally used for the measurement of particulate matter, because of their microscopic size and negligible contribution to total mass. A nanoparticle is of similar size to a virus, and is thousands of times smaller than a human hair. In order to detect their presence it was necessary to use advanced instrumentation and techniques which have only recently become available following the development of nanotechnology. Consequently, the research required to be conducted with dedicated sampling and measurement equipment rather currently available, not only in Italy but in the whole of Europe, and whose utilization in the investigation of stationary combustion processes has very limited application reported within the current scientific literature. The results of the study represents thus an important contribution to the enlargment of knowledge in a field still poorly investigated, and on which in Italy there has recently been much speculation without any reference to scientifically reliable data.

1.1 Organization and working group

The study involved three years of work and encompassed the most significant aspects of the topic:

1. critical analysis of available scientific literature and data regarding the formation and emission of fine particles as well as their potential effects on human health;
2. experimental investigation for the evaluation of emissions from stationary combustion sources, specifically for domestic heating activities and waste-to-energy plants;
3. experimental investigation for the evaluation of fabric filter capture efficiency for ultrafine particles fraction;

4. experimental investigation for the chemical characterization of ultrafine and nanoparticle size fraction emitted by waste-to-energy plants.

Given the broad extension of the scientific knowledge required for addressing such a complex issue, the working group included specialists from a wide range of disciplines and academic sectors:

- Prof. Stefano Cernuschi and Prof. Michele Giugliano, full professors of *Environmental Engineering and Air Pollution,* respectively, School of Civil, Environmental and Land Planning Engineering, Politecnico di Milano;
- Prof. Stefano Consonni, full professor of *Systems for Energy and the Environment* and Prof. Aldo Coghe, full professor of *Propulsion,* Dept. of Industrial Engineering, Politecnico di Milano;
- Prof. Agostino Gambarotta, full professor of *Thermal and Hydraulic Machinery,* Dept. of Engineering, University of Parma;
- Prof. Enrico Bergamaschi, full professor of *Occupational Medicine,* Dept. of Medicine, University of Parma;
- Prof. Pietro Apostoli, full professor of *Occupational Medicine*, Dept. of Medicine, University of Brescia.

Other members included research and laboratory assistants from LEAP and Politecnico di Milano: Senem Ozgen, Matteo Perotti, Giovanna Ripamonti, Giovanni Sghirlanzoni, Ruggero Tardivo.

The group and the experimental activities were coordinated by Prof. S. Cernuschi, Prof. S. Consonni and Prof. M. Giugliano.

2 REVIEW OF GENERAL SCIENTIFIC FRAMEWORK

The aim of the first phase of the study was the identification of a comprehensive framework of the scientific knowledge available in a filed that, relatively new and fast growing, is still poorly investigated and, partly for this reason, the subject of misunderstandings and misconceptions. This was achieved by means of a wide literature survey of national and international studies and reports available within the reference scientific international context, critically analyzing and reviewing all the various implications and issues associated with the emissions of ultrafine particles:

- Phenomena involved in their presence in emissions and the atmosphere;
- measurement techniques;
- control technologies;
- sources and inventories;
- health effects.

The resulting picture reveals, firstly, the complexity and extreme difficulty of describing all the characteristics of the processes of formation, diffusion, transportation and atmospheric conversion of ultrafine particles and their health effects. On the other hand, the significant lack of available data, models and measurement techniques makes rather

difficult, even within a conservative approach, the identification of proper intervention strategies for restricting or regulating any particular source of ultrafine particles.

It has long been known that, alongside natural sources, combustion is one of many human activities which emit ultrafine particles. However, there is still at present no documented evidence for any relationship between specific technologies of stationary combustion and the presence of ultrafine particulate in the atmosphere, or for a link with health effects resulting from exposure of the population. As with almost all pollutants affecting air quality in large urbanized areas, at the moment only a general indication can be expressed regarding traffic, which certainly represents a significant source.

3 CHARACTERISTICS OF ULTRAFINE PARTICULATES

Figure 1 shows the typical size range of different particles and solids of various origin. Although this is an issue that is still subject of discussion, the convention of defining ultrafine particles (UP) as solid or liquid agglomerations of less than 100 nanometers (1 nanometer = 10^{-9} m) and nanoparticles (NP) as agglomerations smaller than 50 nanometers (Figure 2) is gradually being adopted by the scientific community. This is a completely arbitrary distinction, since there is not any clear discontinuity between the sizes of single atoms or molecules and larger and larger agglomerations. Other authors apply the same definition as above to different size ranges, though they still maintain the upper limit for ultrafine particles at 100 nm.

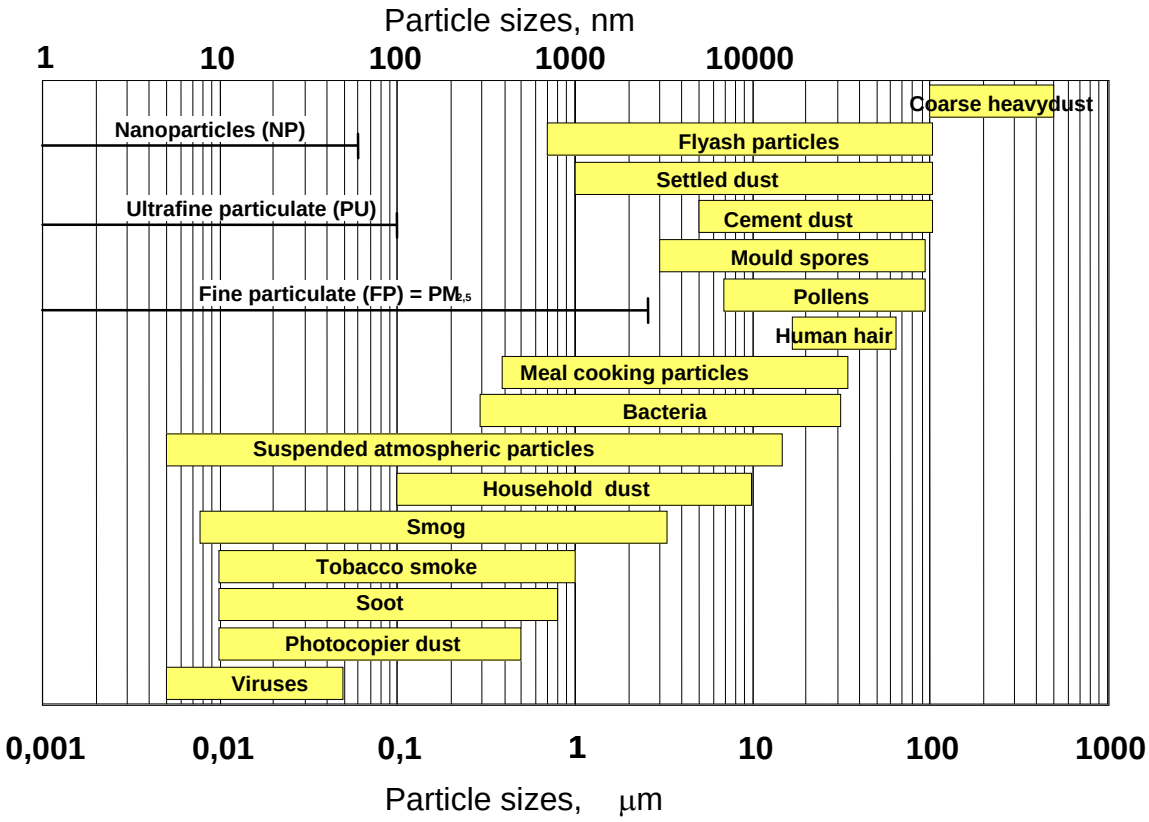


Figure 1: *Typical size range of atmospheric particles of different nature and origin.*

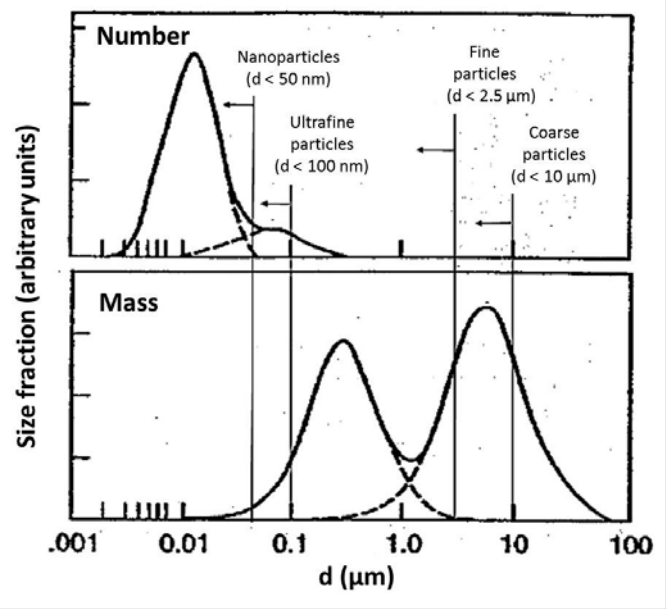


Figure 2: *Typical mass and number size distribution of atmospheric particulates.*

There are significant numbers of ultrafine particles deriving from natural processes and human activity suspended in the atmosphere (Figure 3). Both naturally-occurring particles and those resulting from human activity depend on so-called primary contributions, i.e. particulate emitted as such by the source, and secondary contributions, resulting from formation processes in the atmosphere involving gaseous precursors emitted by the sources.

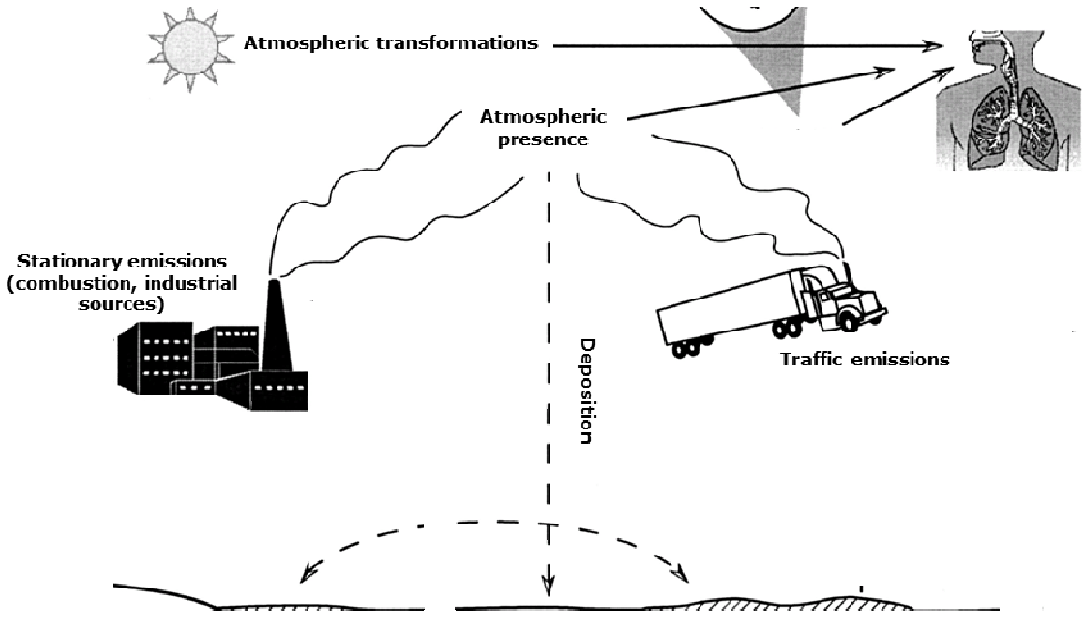


Figura 3: *Schematics of environmental presence and fate of ultrafine and nanoparticles*

Interest in the ultrafine fraction arises from the fact that the latter, because of the particles' very small size, have very different properties from those of the total mass (consisting almost solely of larger particles), essentially attributable to their number and much higher specific surface area. And just as this particular characteristic originates very specific behavior exploited in the field of nanotechnology, it is likely that health effects may be different from those associated with coarser dust. The epidemiology of suspended particulate, and current regulations resulting therefrom, are all based on presence in the atmosphere measured in terms of mass concentration which, given the strong relationship between concentration levels and health effects, is certainly a reasonable indicator of toxicity. However, there are rising concerns about the analogous representativeness of mass concentrations for the effects of the ultrafine component, which might act not in proportion to its mass, which is negligible, but to the number of particles and their specific surface area. In this case, health effects would not be fully represented by conventional measures of particulate matter, and consequently strategies adopted to reduce emissions of the coarse (PM_{10}) and fine ($PM_{2.5}$) components may be ineffective for the ultrafine component.

4 MISCONCEPTIONS AND SCIENTIFIC EVIDENCE

Although it has been known for some time that combustion can generate UP comprising agglomerations of carbon or combustion ash components, interest in the health implications of UP has been focused mainly on work environments featuring high-temperature processes (typically welding). This was the case until rapid developments in nanotechnology, implying the production, manipulation and circulation of large quantities of nanomaterials, brought this issue to the fore, leading to the emergence of inevitable concerns regarding environmental implications and potential risks involved in the dissemination of new kinds of synthetic substances. These concerns, legitimate and justified, in some sectors of public opinion have raised somewhat irrational or even catastrophic fears, such as to result in a request for a moratorium on the development of this important field of science and technology. Unlike the situation in all other countries, where this debate has given rise to further research, in Italy some members of the environmentalist movement have focused their attention on refuse incineration, postulating a direct link between waste combustion and the supposed effects of UP on health. Like all other forms of combustion, waste incineration certainly plays a role in the ultrafine issue; however, the knowledge framework which emerges from this study highlights the fact that to date there is no scientific evidence, either conclusive or suspected, such as to rule out this technique of waste disposal and energy recovery due to the presumed role of emissions as regards the presence of fine particulate and nanoparticles in the atmosphere.

5 ULTRAFINE PARTICULATES IN THE ATMOSPHERE

The content of UP in the atmosphere is inherently unstable due to a series of complex processes that modify the number and sizes of particles: nucleation, coagulation, condensation and evaporation. In addition to the primary inputs, i.e. the UP already present as such at the moment of release into the atmosphere, a fundamental role is played by the weather, the quantity of particles already existing and previous emissions of gas, i.e. those components which precede the formation of new particles. As already mentioned, UP is generally defined in terms of numerical concentration; its contribution to the total mass of solid particulate is in fact of little significance, while the number of particles is much larger (roughly speaking, UP can comprise more than 80% of the total number of solid particles).

Typical concentrations of UP detected and measured in different characterized areas fall within the range of 10-10^3 particles/cm^3 in rural and coastal areas, 10^4 particles/cm^3 in urban areas and 10^6 particles/cm^3 in roadside areas with high traffic density (Figure 4). In the outside air, the number of UP clearly follows typical seasonal and daily patterns. Winter concentrations are generally higher than those in the summer. During the day there is an increase during the morning and evening hours, mainly linked to rush-hour traffic peaks. Another peak sometimes observed shortly after 12.00 suggests the contribution of photochemical reactions. Single 'episodes' of varying length show that certain size fractions increase by one order of magnitude or more. The few available studies on chemical composition show that organic carbon is the dominant element (30 – 75%); depending on the emission source and weather conditions, others are elementary carbon (3 – 15%), nitrates (1 – 20%), sulfates (1 – 20%), oxides of metallic elements (10 – 20%). The processes of photochemical secondary formation could influence this picture significantly following the condensation of organic substances on nuclei of a different nature.

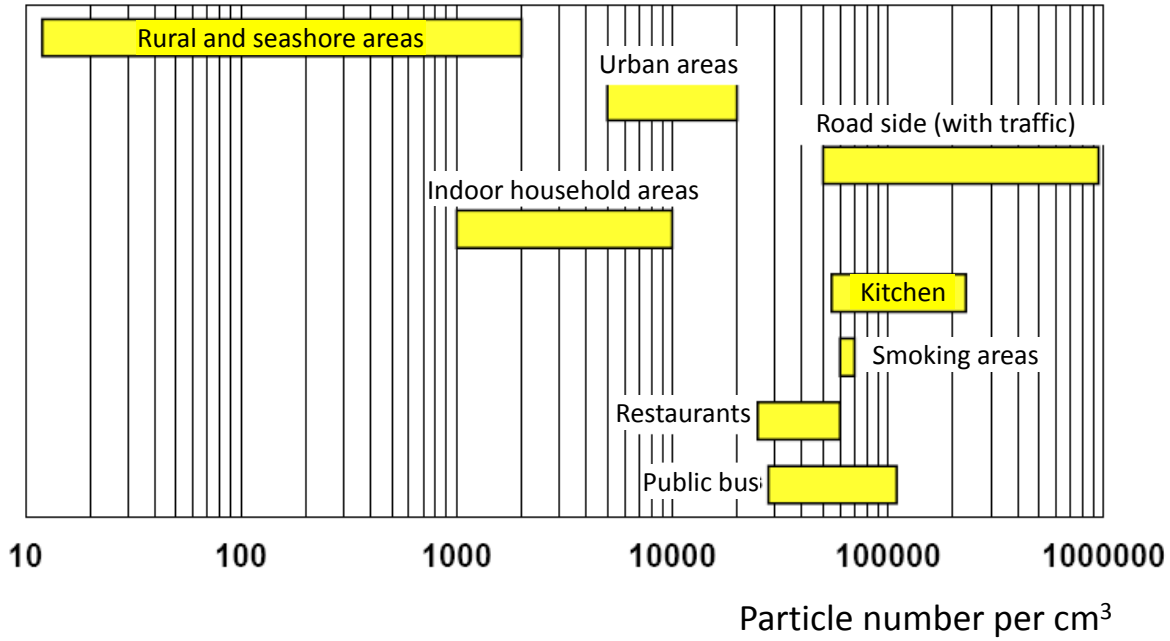


Figure 4: *Presence of UP measured in the atmosphere*

In large urban areas, where the population is most exposed, the most significant source of UP is generally mobile combustion (traffic); in addition the use of biomass in small plant for domestic heating is a significant factor in some areas. The typical average range of the mode of the diameters is 0.02-0.04 μm, similar to that typical for traffic but with a less marked mode due to the simultaneous presence of multiple sources.

In homes, the presence of UP is estimated as being 10^3-10^4 particles per cm^{-3}. In the absence of filters or treatment of the outside air, a substantial contribution is made by particles from the outside atmosphere. However, the indoor environment is generally sealed with respect to particulate pollutants so that in the absence of significant indoor sources, the concentration of UP is lower than that measured outdoors. This is highlighted by studies carried out in some urban and rural sites, which reveal indoor levels which vary greatly but which are systematically lower than the outdoor concentrations, with higher concentrations in urban areas compared with rural areas, and with higher values being recorded in locations more directly influenced by traffic fumes. Furthermore, the size distribution of the particles present indoors is notably different from that outdoors, with the concentration of smaller particles decreasing more significantly and the maximum concentration shifting towards larger diameters. All this can change significantly in the case of notable indoor sources, such as cigarette smoke, the cooking of food, wood-fired heating, candle flames, cleaning procedures.

6 EMISSION SOURCES

Although there are many natural sources of particles that can reach micrometric sizes, the smaller particles seem to originate mainly from human activities. The sources identified are classified as follows.

6.1 Indoor non-industrial environments

The presence of UP in various micro-environments is certain, with higher values where combustion processes take place. In terms of diameter d, typical sizes for sources in indoor spaces are: d~0.01-1μm (cigarette smoke), d~0.03-3 μm (burning candles), d~0.3-0.6 μm (use of aerosols), d~0.02-0.5 μm and d~30-100μm (frying of meat).

6.2 Industrial environments

In the workplace, most PU forms due to nucleation in products of combustion or in saturated steam generated by processes such as welding, smelting and processing of metals, laser cutting, polymer fumes, heating of waxing products. UP may also be generated during mechanical processes, such as high speed grinding, cutting, cleaning. Presumably an increase in nanotechnology applications (including their use for biomedical purposes) will lead to increased exposure to FP and UP.

6.3 Combustion in motor vehicles

Emissions of NP and UP from mobile sources are very much dependent on the type and configuration of the engine, the characteristics of the fuel used, the way the vehicle is used and by the presence and type of specific engine technology and exhaust fume purification devices. The main indications on expected emission levels, based on available information and on numerous experimental studies of and measurements of diesel vehicles especially, can be summarized as follows.

- The evolution of engine technology has led to significant changes in the nature of particulate emissions, in particular to an increase in the volatile fraction. Most UP and NP are composed of condensed volatile types, with sulfur and heavier hydrocarbons which comprise the main precursors in the formation processes of condensation nuclei.
- The particulate emitted by an internal combustion engine is intrinsically bimodal. The variation in the concentration (by number) of particles with their size can be expressed as a linear combination of two log-normal distributions: one centered at 0.08-0.12 μm (accumulation particles) and the other at 0.02-0.03 μm approx. (nucleation particles). The relative weights of the two distributions depends on engine technology, fuel and lubricant characteristics, conditions of usage and the degree of wear of the engine, weather conditions, and last but not least, the sampling procedure and the method of measurement adopted.

- The devices for the control of particle emissions adopted in vehicles with diesel engines (diesel particulate filters) can reduce the ultrafine particles by over two orders of magnitude (Table 1, Figure 5), while performance is not the same as regards nanoparticles. Filtration captures the solid particles which would act as condensation surfaces for heavier volatile elements very efficiently, thus contributing to the formation by nucleation of new nanoparticles and their subsequent increase;
- During filter regeneration, which takes 20-30 minutes, there is a notable increase in NP emissions. However, this phenomenon has a limited influence on overall emissions, given that regeneration takes place on average approximately every 500 km.
- Gasoline direct injection (GDI) engines emit levels of nanoparticles which are higher by almost two orders of magnitude compared to both indirect injection engines and diesel engines with a particulate filter.

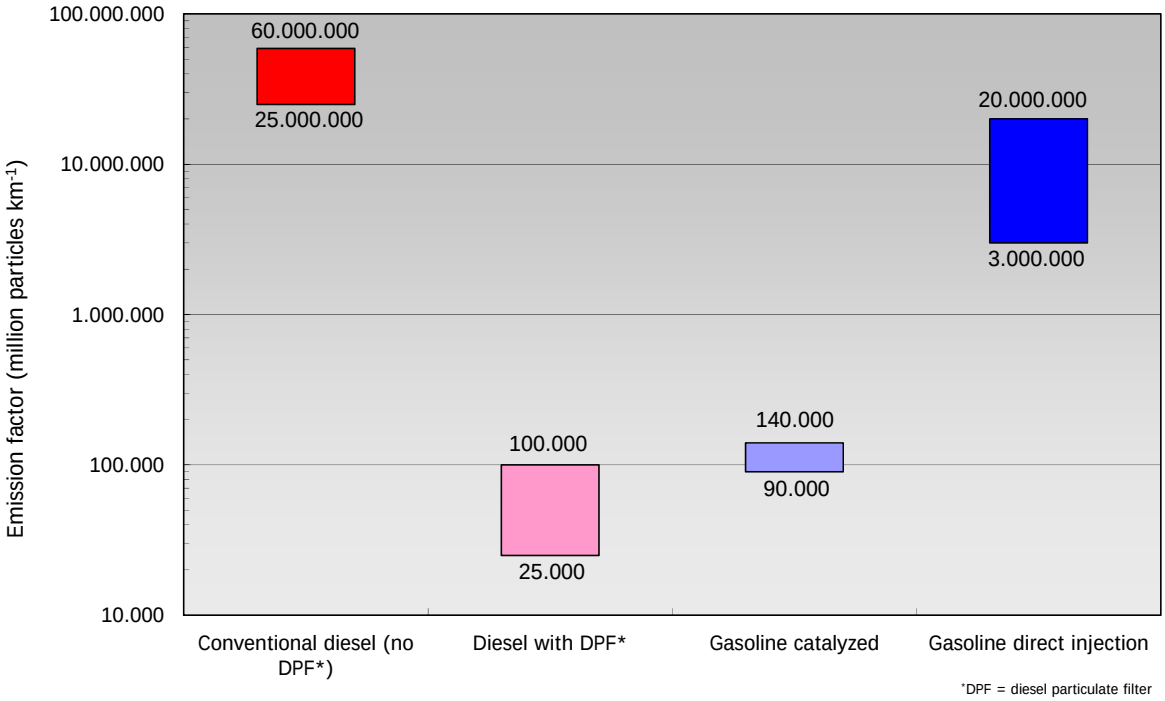


Figure 5: *Presence of ultrafine particles measured in exhaust emissions from light-duty vehicles.*

Type of vehicle	Emissions (number of particles per cm^3)
Traditional diesel without particulate filter	21,000,000 – 43,000,000
Diesel with particulate filter	10,000 – 500,000
Traditional catalyzed gasoline/petrol	90,000 – 270,000
Direct injection gasoline/petrol	4,000,000 – 17,000,000

Table 1*: Concentration range of UP measured in exhaust emissions from light duty vehicles along representative driving test cycles.*

For diesel engines, the main features of the emission reveal particulate consisting of carbonaceous material generated by pyrolysis of the fuel, on which are adsorbed various kinds of organic compounds. The sizes fall into different intervals depending on the prevailing formation mechanism: nucleation or accumulation. The nucleation particles are the smallest (d~0.007-0.04 μm), with a small fraction made up of carbonaceous and metallic ash originating from the lubricant, while those from accumulation are made up of solid carbon nuclei onto which condense hydrocarbons, sulfates, nitrates and metallic ash, with diameters typically between 0.04 and 1 μm and a concentration peak between 0.1 and 0.2 μm. In addition to the organic particles originating in the combustion chamber through nucleation or accumulation there are metallic particles originating from wear of mechanical parts and carried by the lubricant oil. Otto indirect injection gasoline (petrol) engines emit particles with a distribution that tends to be asymmetric and with an average diameter of 0.04-0.08 μm. Although the size distribution is different, the emissions from direct injection engines when running under homogeneous loads are similar, while direct injection engines under stratified load appear to emit almost 100 times more particles (Figure 5). Natural gas engines generate primary particles measuring 0.02-0.03 μm, similar in all respects to those generated in diesel engines; the number of accumulation particles measuring 0.1 μm is of the same order of magnitude as those emitted by a diesel engine fitted with a DFP, while the number of UP seems to be even higher. Finally, in two-stroke engines the particles emitted at the exhaust mainly comprise condensed oils, with the formation of accumulation particles (0.06-0.09 μm) originating in the combustion chamber at high temperatures seemingly determined by the presence of lubricant.

A large fraction of the gaseous precursors generally condenses or adsorbs on the surface of the primary carbon particles, thus contributing to the accumulation phase. However, if the concentration of primary carbon particles is low and therefore the available surface for adsorption is reduced, the volatile substances give rise to nucleation in homogeneous phase, thus generating volatile NP. This phenomenon is enhanced in DFP diesel engines, where accumulation is much reduced by particle filtration; hence there is an increase in nucleation. A high number of accumulation particles has the opposite effect, so that older and more worn vehicles, which generate large quantities of primary particulate, give rise to a lower level of nucleation.

A higher number of NP are formed on cold starting and with heavy loads, or with rapid acceleration or high vehicle speeds. With low or medium acceleration emissions from an indirect injection gasoline/petrol engine are about half those of a DFP diesel. However, when acceleration is rapid or speed is high, petrol/gasoline engines may emit more than diesel due to condensation of non-combusted volatile fuel present when running on a richer mixture.

6.4 Combustion in stationary sources

The data available indicate average concentrations of UP at emission of 10^6-10^8 particles/cm^3 for solid (coal, biomass) and liquid fuel boilers; 10^5-10^6 particles/cm^3 for the very few studies so far carried out on incinerators; approx. 10^3 particles/cm^3 for gas turbines (Figure 6). The comparison is only indicative, because emissions are heavily influenced by fuel type, combustion technology, particles removal systems (filters) and the operating conditions of the plant; in addition to the above, results are influenced by the sampling system and particle counting methodologies, especially the ability to capture and measure condensable semivolatile components. The size distribution and the number of particles are influenced by the presence of SO_2 and the thermal load. In natural gas combustion, the number of particles smaller than 0.01 μm decreases by three orders of magnitude on halving the thermal load of the boiler compared to nominal conditions, while a corresponding variation is not observed for particulate measuring more than 0.1 μm. For fuel oil, vice versa, load reduction reduces the number of d~0.1μm particles, without any apparent variation in those with a diameter of less than 0.01 μm, which are more or less constant in all operating conditions. Wood burning in domestic fireplaces produces a unimodal size distribution with a maximum of about 0.17 μm, while particles smaller than 0.1 μm have been observed in household wood-burning boilers. The quantity and types of salts of alkaline metals generated during combustion, and so the possible generation of UP, depends on the composition of the biomass.

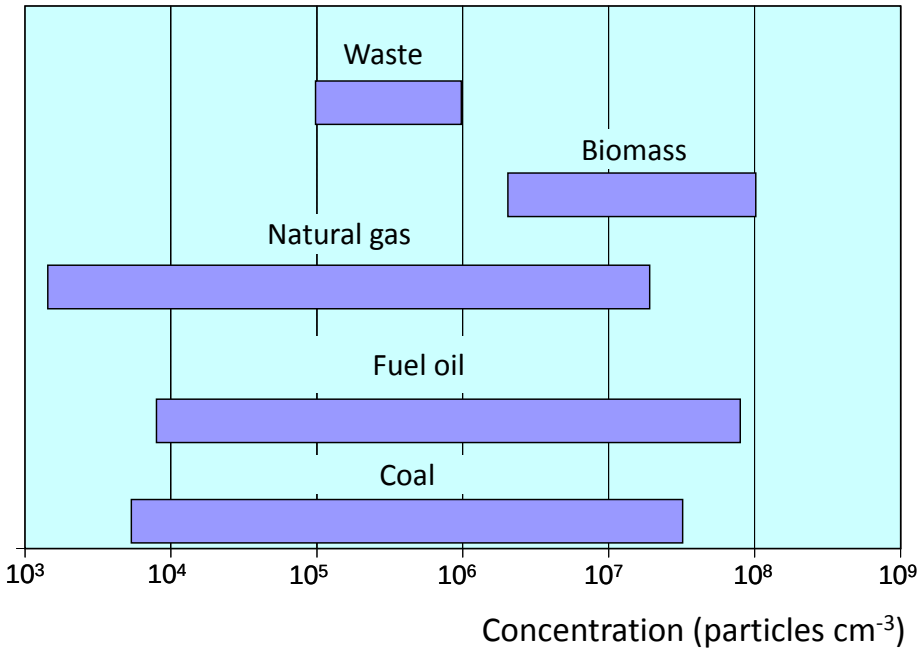


Figure 6: *Approximate intervals of UP concentration levels in emissions from stationary combustion (Data from present investigation not included)*

7 CONTROL TECHNOLOGIES

Devices for the control of particulate emission are now standard equipment for the majority of systems and plant involving combustion processes. This is especially true for large stationary plant, in which some system for the reduction of particles emission is compulsory, with the exception of plant fuelled by extremely 'clean' fuel such as natural gas.

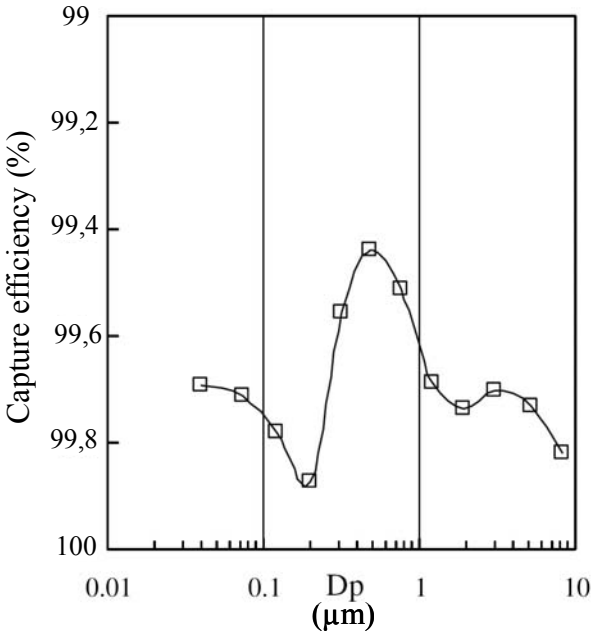
7.1 Stationary sources

For stationary combustion plant, the best commercially available technology for controlling the emission of particles are fabric filters (baghouses) and electrostatic precipitators, which can guarantee removal efficiency of more than 99%. Performance measurements for fine particulate reveal the superiority of filters in guaranteeing observance of the most restrictive measures, with the possibility of achieving concentrations of less than 1mg/m^{-3}. The removal of ultrafine fractions and nanoparticles, although widely described by means of theoretical models which emphasize the role of the main elementary mechanisms active in capture, has not yet been fully documented. Investigations are generally limited to the sector of the combustion of solids in thermoelectric power stations and different kinds of boilers. Only very limited information is available on waste incineration. Moreover, the efficiencies observed are often reported in terms of mass and not number of particles, making it especially difficult to evaluate the performance of different devices. Nevertheless, the general indications which emerge for the best available technology basically confirm the well-known trends of the granulometric efficiency of separation, with a reduction in levels of removal for size classes between 0.1 μm and 1-2 μm. For this size range, the reduction in capture efficiency is directly related to inertia and diffusion mechanisms responsible for particle capture. For the ultrafine fractions and nanoparticles, situated below the lower limit of this range, both electrostatic precipitators and fabric filters maintain their high levels of capture. The separation performance, at least for sizes up to a few tens of nm, thus appears to be in line with that for coarser material, with capture levels for units which are of the correct size and properly maintained are between 97 and 99% of the total number of particles.

The general efficiency trend also shows how fabric filters are potentially less subject to reduction in capture levels in the aforementioned range of 0.1-1 μm, with removal which is thus much more uniform and better across the whole size range than that typical of electrofilters. An example of this behavior is shown in Figure 7, which highlights separation yields for UP and nanoparticles of more than 99.5%, with no significant change with respect to the values recorded for coarser fractions (d > 2.5 μm).

Finally, available information does not reveal any particular developments in innovative equipment, while appreciable efforts have been made in improving already-consolidated technologies, with intervention involving device configuration (hybrid

systems, wet electrofilters) and/or mode of operation (low-pressure centrifugal systems, power supply voltages for electrofilters).



Yi H. et al., *Fuel* (2008)

Figure 7: *Particle size removal efficiency by number measured for a fabric filter (baghouse.*

7.2 Motor vehicles

In the field of mobile combustion, in recent years engine manufacturers and automakers have developed ever more efficient systems for the reduction of pollutants. Given that pollutant emission limits are expressed in terms of mass discharged (and not the number of particles), all research and development efforts in the industry have been aimed at limiting the mass of particles emitted. As already mentioned, for UP this is very low. To date therefore there are no specific solutions aimed at reducing the formation of FP and UP in gasoline or diesel engines. Commercially-available technologies for limiting emissions of carbonaceous particulates (diesel soot) and NO_x are not particularly effective in reducing nanoparticle emissions (especially for particles smaller than 0.01 μm); on the other hand, they give very promising results as regards the removal of larger particles and particulate precursors.

These types of intervention operate simultaneously in three directions: the development of innovative engine technology (especially regarding cylinder filling, injection and combustion), the adoption of post-treatment systems, and intervention regarding the fuel. The use of fuel which is virtually sulfur-free results in a reduction in the precursors of enucleation processes and so of NP, especially at high loads. Currently, however, the main contribution to reducing particulate is provided by exhaust cleaning systems, which can be grouped into two main categories: catalytic convertors and particulate traps.

Catalytic convertors are able to act only partially on ultrafine particulate, except as regards the reduction of the organic component (oxidizing catalysts) and of NO_x, which are one of the most important precursors of secondary particulate. Although the advantages of using catalyst substances are obvious, some problems relating to them can be highlighted.

The removal of diesel soot particles present in exhaust fumes can be achieved by means of filtering with exhaust filters known as 'diesel particulate filters' (DFP). The particles are trapped in the pores of the filter and then oxidized (by heat or catalyst), thus 'regenerating' the filter. Regeneration involves the burning of the soot particles, triggered by post-injection of fuel which temporarily increases the temperature of the gases (normally to over 600°C), thus permitting oxidation of the carbon. The process is controlled automatically by the engine, which starts regeneration at set distances (every 400 – 500 km) or when excessive counter-pressure is detected at the exhaust.

8 HEALTH EFFECTS

Evidence regarding possible health effects resulting from or associated with exposure to FP and UP are primarily derived from epidemiological and toxicological studies. The former concentrate on the link between the concentration of particles in the atmosphere (which need not necessarily correspond to individuals' exposure) and critical

effects: mortality, morbidity, acute effects, effects in susceptible populations (children, the elderly), etc. The latter, mainly experimental, aim to further understanding of the biological mechanisms by which exposure to particles may determine adverse effects on the organism.

8.1 Epidemiological approach

The most authoritative evidence of premature mortality, both general and due to specific causes, comes from studies conducted in the USA, Europe and Italy. However, of these, only that carried out in Erfurt in Germany measured UP (0.01-0.1 μm), finding a relative risk (RR) of total mortality of 1.023 – 1.031 for cardio-respiratory death with an average increase in the number of UP of 9748/ cm^3.

Studies based on time series have investigated acute effects correlated with daily changes in the levels of FP ($PM_{2.5}$) e UP ($PM_{0.1}$). The main findings can be summarized as follows: (i) FP/UP have a weak effect on both total mortality and respiratory and cardiovascular mortality; (ii) FP tends to be associated with immediate effects (latency of 0 – 1 day), mainly respiratory, and UP with relatively delayed effects (latency of 4 – 5 days), mainly cardiovascular; (iii) the effects of the two fractions, where measured, are independent. From this observation it follows that the amount of FP cannot be used as an indication of exposure to UP.

Although it is not possible to isolate the effects of UP from that of other pollutants, some short-term effects on susceptible groups (especially patients with chronic cardio-pulmonary diseases) seem to be associated with or sporadically correlated with exposure to UP: aggravation of respiratory and cardiovascular diseases, increased consumption of asthma medication in the days following increases in the concentration of UP; increase in symptoms (cough) and changes in respiratory functional parameters in asthmatic adults; heart rhythm changes; increased risk of cardiac ischemia during exercise in patients with stable coronary artery disease; changes in coagulation and biochemical markers; reduction in number of active days; variations in heart rate of patients with chronic coronary artery disease. Studies carried out in Rome have revealed statistically significant associations between coronary artery mortality, particularly in the elderly, and the number of UP, PM_{10} and CO from mobile sources. Finally, the European study 'ULTRA' suggests that UP does not seem to account for the acute effects attributable to FP; but it does partly explain the effects of traffic fumes.

The more obvious role of UP compared to FP in the association with cardiovascular disease mortality and morbidity is consistent with our current knowledge of their action mechanism, which includes the activation of receptors sensitive to irritants and the genesis of an inflammatory response in the respiratory tract, the hypothesized passage of UP through the epithelia, the activation of vascular endothelia. However, the (three) main studies specifically evaluating the role of the number of UP indicate the significant role of exposure to co-pollutants, in particular gaseous species like CO and NO_2.

Ultimately, the absence of measurements of exposure over sufficiently large populations and the difficulty of reliably reconstructing individuals' exposure (including that to indoor sources) lead to the conclusion that the evidence given above is very weak and that RR (which reach but do not exceed 1) are of statistically limited significance. In any case, in not one of the few studies dedicated to UP is there any specific reference to activities involving waste-to-energy incineration, nor is mention made of any particular hazardous role it may have compared with other forms of combustion or sources of emission in general.

8.2 Toxicological approach

There is now accumulated evidence regarding the effects of particles generated by diesel engines, welding fumes, soot, and fly ash nanoparticles. Available toxicological studies consider oxidative stress in the production of reactive oxygen intermediate, which is the main mechanism responsible for the toxic effects of inhaled UP. The cascade of events may differ depending on the type of particles, but the final effect is still an inflammatory process.

Size alone is not enough to condition toxicity, although it does result in an inflammatory response of greater magnitude compared to FP with the same chemical composition, mass being equal. Given that for equal masses the total surface area of an aerosol consisting of UP is much greater, the particles have a higher probability of adsorbing and transporting organic and inorganic toxic substances on their surfaces. Chemical composition, especially an abundance of aromatic compounds and transition metals, the presence of bacterial or viral contaminants, chemical reactivity, the solubility of the components (which in turn influences persistence) are fundamental in determining the level of toxicity. Variability in these characteristics would explain the variability of health effects observed in different areas.

Experimental studies conducted on animals, and clinically-controlled tests on humans, suggest that the ability of UP to induce adverse effects is greater than that observed following exposure to larger particles. Furthermore, these studies have not clearly demonstrated the passage of insoluble particles through the lung barrier and diffusion in systemic circulation, which is believed to be quantitatively very limited.

The link between exposure to air-borne particulate and cardiovascular mortality involves a pathogenic process that includes lung inflammation induced by the particles, systemic inflammation, accelerated atherosclerosis, and alteration of the autonomic nervous system's control of the heartbeat. Together with epidemiological observations, evidence is emerging that exposure to particulate matter, no matter what size fraction, is associated not only with the aggravation of pre-existing disease, but represents a real risk factor for the development of chronic degenerative diseases. In this context it would be extremely desirable to isolate the effect of particles from that of other pollutants, but this is generally impossible. In the majority of studies the effect of UP is inseparable from that of other co-pollutants generated by traffic (NO, NO_2, and CO) and that of FP.

Since pollution from UP is only one aspect of the more complex problem of atmospheric emissions related to human activity, it seems simplistic to focus on the presence or the effects of a single class of pollutants; in addition some studies, conducted in some cases in Italy, indicate the contribution of weather and climatic variables which facilitate the conversion from gas to aerosol, the aggregation and the long-distance transportation of UP.

To summarize, while attention should be paid to the environmental role of ultrafine particulate and its components, no indication emerges from analysis of the toxicological implications of studies in this area, of special risk which can be attributed to UP from the incineration of waste with energy recovery, if this is carried out in line with best available technology.

9 EXPERIMENTAL INVESTIGATION

Analysis of current knowledge was carried out simultaneously with the purchasing of instrumentation and the designing of experimental campaigns planned for the next phase of the study. Measurements were taken to determine the concentrations of Ultrafine Particles (UP) and Nano Particles (NP) in the products of combustion generated by:

- biomass boilers for domestic heating;
- oil-fired boilers for domestic heating;
- natural gas boilers for domestic heating;
- low-capacity closed wood-burning fireplace;
- large waste-to-energy plant, specifically three plants built in the last decade, technologically in line with best-available technology.

The survey also covered the evaluation of the capture efficiency of fabric filters regarding ultrafine components and nanoparticulate, and the chemical characterization of the fractions emitted by waste-to-energy incineration.

In line with the characteristics of the matter to be identified, the presence of particles in combustion products was measured in terms of their number per unit volume (number of particles per cm^3), instead of the usual mass concentration (mg per m^3); mass concentration in this case is not very significant because:

- the amount by weight of matter in emissions is generally not significant, with levels generally below the detection limits of sampling and analysis protocols available for fine particulate; this renders measurement to an acceptable level of accuracy very difficult;
- alleged health effects do not seem to be related so much to mass, which is minimal, as to the number of particles which, because of their size, may penetrate deep into the respiratory tract.

Fumes emitted into the atmosphere by combustion plant running on fossil fuel, wood and generally any matter containing carbon and hydrogen (such as waste) contain chemical species in gaseous state which when cooled and diluted by the ambient air, give

rise to nucleation and condensation processes which generate more ultrafine particles and nanoparticles. These processes typically take place in the atmosphere, after the fumes have been released by the plant chimney. The ultrafine particles thereby generated makes up the condensable or 'secondary' fraction, which is in addition to the 'primary' fraction comprising the particles already present at the point of emission. The quantity of secondary ultrafine particles may be considerable, hence the need to take it into account in order to make a proper evaluation of the emissions from a given plant or process. This requires a dedicated sampling and analyzing system, with specific sampling procedures, aimed at simulating the phenomena of nucleation and/or condensation of volatile and semivolatile species at the moment of emission into the atmosphere, combined with devices able to measure the number of particles to sizes approaching tens of nm.

Naturally, once UP has been emitted into the atmosphere and after secondary formation processes near the source have ended, it is transported and diffused in the atmosphere, during which time processes of nucleation and condensation may continue. In addition, phenomena of coagulation, agglomeration, transformation and interaction with other species, and removal by obstacles, may occur to different degrees. This complex process makes it particularly arduous to determine the role of the sources in the actual presence of UP in the atmosphere. On this last problematic issue, which is beyond the scope of this study, knowledge is still very partial and fragmentary, to the extent that the (possible) connection between emissions and presence in the atmosphere is at present very vague and uncertain.

10 MEASUREMENT CAMPAIGNS

10.1 Instrumentation

In line with the measurement requirements outlined above, the sampling instrumentation adopted in the survey was designed and assembled for measuring ultrafine particulate in combustion gases both at emission and after dilution. Measurements carried out on 'emission state' combustion gas are by convention called 'hot gas' measurements, while those on diluted gas are known as 'cold gas' measurements. This implies that 'hot gas' measurement measures UP as it is emitted by the process, while 'cold gas' measurement reveals the number of UP after nucleation and condensation of the semivolatile fraction and following cooling and dilution with ambient air previously treated with an absolute filter.

Investigation thus required the assembly of a complex system of sampling and measurement, briefly described below. The line has a modular structure (Fig. 8) comprising sampling equipment which, set up in accordance with the EPA CTM-039 method, includes a probe equipped with centrifugal separators for retaining matter larger than 2.5 μm and a dilution section where fumes mixed with filtered and conditioned air remain in a residence chamber for appropriate periods of time. The entire system is monitored and controlled by software, which regulates its operation through a control unit.

The line is also fitted with a multi-stage Electrical Low-Pressure Impactor (ELPI) supplied by Dekati Ltd (Finland) for real-time measurement of size distribution and concentration by number of airborne particles in the range 0.007 µm - 10 µm.

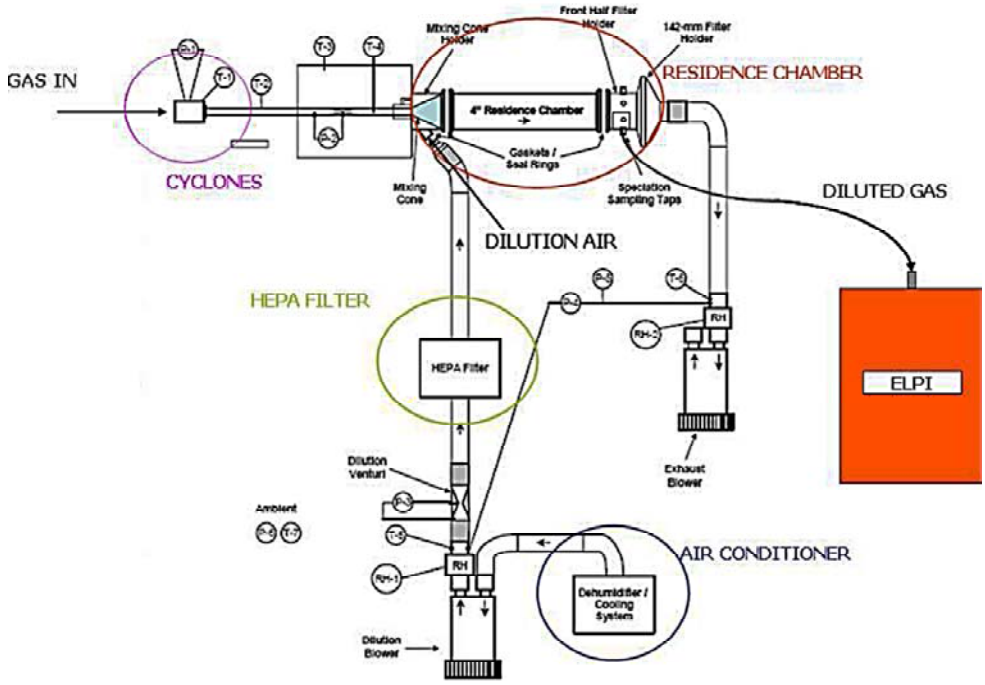


Figure 8: *Diagram of sampling and dilution line*

10.2 Emissions measured

The survey of emissions from waste-to-energy incineration of urban refuse involved the three pants in Milan, Brescia and Bologna, which are typical of the most up-to-date high-power installations in the current technological context and are equipped with air purification systems in line with best available technology (BAT) in the field for drastic control of conventional pollutants (particulate, acid gases, nitrogen oxides) and trace substances (metals, dioxins). Campaigns on plant for producing thermal energy for domestic use, developed at the laboratories of the Stazione Sperimentale per i Combustibili (Experimental Station for Fuels), evaluated the combustion of wood, oil and natural gas in a medium-size boiler (100 – 150 kW design rated heat output), using respectively an advanced pellet-fuelled boiler equipped with an axial cyclone for particulate removal, a low-power (11 kW) wood-burning closed fireplace and a unit with a burner fuelled by oil and natural gas, typical of currently-used domestic boilers. The set of tests included cold measuring, carried out over varying dilution ratios across the whole range allowed by the probe, integrated with hot sampling, aimed at identifying the contribution of the condensable component and conducted with a heated sampling probe. The latter, with identical configuration to that used for the cold sampling, directs combustion gases to the impactor with no preliminary dilution. Evaluation was also extended to the presence of UP in the area where the plants are located, with

measurements of the concentration levels of particles in the ambient air, in order to assess their role regarding the amounts measured for plant emission. These concentrations are indicated in the tables under 'ambient air'.

Assessment of the capture efficiency of the fabric filter was carried out on an experimental line comprising pilot-scale equipment fed with a gas flow deriving from the main line of an industrial-waste incinerator, after addition of the mixture of neutralization and adsorption additives and before entry into the plant's fabric filter. Data acquisition was carried out in normal plant operating conditions using cold sampling, both before and after the filter, to determine capture efficiency not only as regards primary particles already present in the flue gas, but also regarding the 'formation potential' of secondary particulate, i.e. newly-formed particulate after cooling and dilution in the atmosphere.

Chemical characterization of ultrafine particulate and nanoparticles emitted by waste-to-energy incineration was carried out by means of a series of samples taken over a suitable timespan for the gathering of a sufficient quantity of matter on different media, situated in the individual ELPI impactor dishes specifically for the analytical determination of ions, trace elements, total carbon and total mass.

11 RESULTS

The main results of the overall survey are illustrated in the following paragraphs, with the concentration levels and size distributions of UP and NP broken down by plant type (domestic heating, waste-to-energy incineration). In the description of the results obtained for size distribution by particulate number, the terms 'ultrafine fraction' and 'nanoparticles fraction' indicate respectively the particles with aerodynamic diameter of less than 0.1 μm (100 nm) and 0.05 μm (50 nm).

11.1 Domestic heating plants

The main results of the set of tests carried out on domestic heating plant are summed up comparatively in Table 2, which summarizes the concentration levels and the main size characteristics detected over the whole dilution range adopted in the cold tests and the corresponding hot tests.

The results for pellet boilers at nominal load give average concentration values equal to 4.5×10^7 cm^{-3} at low dilution ratios (RD = 15-20), 4.1×10^7 cm^{-3} for intermediate dilution ratios (RD = 25-35) and 5.2×10^7 cm^{-3} for higher ratios (RD = 40-50). The mode of the distribution is located in correspondence to a diameter of 0.072 μm, with the ultrafine size fraction making up approx. 95% of the total concentration measured. The measurements do not appear to be especially influenced by the dilution ratio, with comparable emission content distributions both in terms of concentration and of size. Compared to nominal operating regimes, samples taken at reduced thermal load reveal a

slight reduction in concentrations, at an average value of 2.4×10^7 cm^{-3}, and a corresponding notable shift in size distribution towards larger sizes: the ultrafine particulate fraction is reduced to 39%, with a simultaneous increase in the mode up to values of around 0.2 μm. Thus the operating of the boiler in these conditions seems to generate a smaller number of ultrafine particles, due to the presence of significant fractions of coarser matter of primary origin, resulting from non-optimal combustion conditions, able to act as condensation and agglomeration surfaces: the increase in size of existing particles is thus favored with respect to the formation of new particles, in accordance with the reduction observed in the concentration levels and with the shift of size distribution toward larger particles. In accordance with results typical for the type of fuel, concentrations measured during hot sampling, carried out on gas without dilution, were higher than the detection limit of the impactor (approx 6×10^7 cm^{-3}). As it was reasonable to expect, particulate levels were clearly higher compared with those measured in the combustion air, which were on average 2.9×10^4 cm^{-3}.

Fuel	Sampling conditions – boiler operating conditions	Concentration (cm^{-3})	Fraction<0,1μm(%)/ Fraction<0,05μm(%)	Mode (μm)
Pellets	Dilution-nominal load Dilution-reduced load	41,000,000 – 52,000,000 24,000,000	93-95 / 19-28 39 / 0	0.072 0.204
Closed fireplace	Hot-nominal load Dilution-nominal load	51,000,000 – 81,000,000 60,000,000 – 78,000,000	48-70 / 9-19 54-72 / 8-19	0.02-0.12 0.02-0.12
Oil	Dilution-nominal load Dilution-reduced load Hot-nominal load Hot-reduced load	8,600,000 – 67,000,000 11,000,000 – 17,000,000 1,300,000 6,000,000	> 99 / 89 - 97 92 - 95 / 40 - 56 97 / 74 94 / 64	0.021 0.072 0.054 0.054
Natural Gas	Dilution-nominal load	4,500	89 / 68	0.021
Outside air	-	15,000 – 28,000	88 / 64	0.021

Table 2: *Comparative summary of results from survey of domestic heating plant*

Analogous results obtained for a closed fireplace results in average concentrations of 6.4×10^7 cm^{-3} in hot tests and of approx. 7×10^7 cm^{-3} in those with cold dilution, with variations of little significance between the different sampling conditions and with dilution level which does not appear to affect significantly measured values obtained with cold sampling measurements Ultrafine particles make up between approx. 50% and 70% of the total number of particles, in both hot and cold tests, with a slight increase as the dilution ratio increases for cold tests, while nanoparticles shift from approx. 10% to approx. 20% as dilution increases; although not influencing significantly number concentrations, dilution thus seems to increase the number of nanoparticles. This behavior seems to be confirmed by the size distributions, which clearly show a bimodal pattern for all test conditions, with the first mode at about 0.02 μm and the second at about 0.12 μm. In

general terms, concentration levels and size distributions are comparable with those obtained for pellet boilers, with emissions also in this case too are much higher than combustion air.

In contrast with wood burning, the levels of particulate measured from oil-fired boiler in nominal load conditions reveal a significant dependence on the dilution ratio used. Concentrations increase from an average of 8.6×10^{6} cm^{-3} for higher dilution ratios (RD = 40-50) to 2.2×10^{7} cm^{-3} for intermediate dilution ratios (RD = 25-35) to 6.7×10^{7} cm^{-3} for the lowest dilutions (RD = 15-20), while no similar changes are observed in particulate size distribution, with ultrafine particles making up over 99% of the total and with mode corresponding to a diameter of approx 0.02 μm for all the dilutions tested. The variations found in the concentrations seem to be due to the effect of the extent of dilution in progressively decreasing partial pressure of the semivolatile components, thereby reducing the formation of new particles through nucleation. Results from hot gas tests, with reveal average concentrations equal to 1.3×10^{6} cm^{-3}, also highlight the role of the condensable fraction on particulate emissions, with an increase in concentrations measured with cold test with respect to hot sampling from 7 times for higher dilutions, up to 52 times for the lowest dilutions. Tests in conditions of reduced load reveal concentrations which are basically independent of the dilution, with more or less stable average values between 1.1×10^{7} cm^{-3} and 1.7×10^{7} cm^{-3}; size distributions results in a shift towards coarser matter, with the ultrafine fraction reducing to 92% - 95% and a corresponding slight increase in the mode, up to as much as 0.07 μm. The results thus seem to confirm those for pellet boilers in indicating that, during non-optimal combustion conditions, there are more primary particles which lead to the prevalence of heterogeneous condensation on already-present nuclei compared to homogeneous nucleation of semi-volatile matter. As already explained for nominal load operation, in conditions of reduced load hot tests reveal increased concentrations associated with the condensable component, which is at lower levels. Finally, in line with expectations for this type of combustion, in all test conditions and for both regimes of boiler operating conditions, concentrations were found to be far higher than those found in the combustion air.

Results for the combustion of natural gas are obviously much lower with respect to the same values measured for the other types of fuel. They reveal an average concentration of 4.5×10^{3} cm^{-3} for a dilution ratio of 15 times, 10 times lower than that in the combustion air, while for higher dilutions the values are below the instrumentation detection limits. Size distribution appears to be heavily conditioned by the presence of ultrafine fraction and nanoparticles, with the mode corresponding to 0.02 μm. The very limited amounts recorded during tests with dilution led to the decision not to proceed with undiluted hot gas measurements.

11.2 Waste-to-energy plants

The main results from waste-to-energy plants are summarized in Table 3, again in terms of concentration levels and of the principal size characteristics found across the dilution range adopted in the cold gas tests and corresponding hot gas tests.

Plant	Sampling conditions	Concentration (cm^{-3})	<0.1µm (%)/ <0.05µm (%)	Mode (µm)
Milan	Dilution Hot Ambient air	10637 - 17228 4958 32059	95 - 97 / 79 - 93 97 / 74 96 / 77	0.021 - 0.072 0.017 0.021
Brescia	Dilution Ambient air	3916 - 7035 13529	91 - 94 / 71 - 82 91 / 70	0.021 - 0.072 0.021
Bologna	Dilution Hot Ambient air	41496 - 70026 25000 19594	95 - 97 / 84 - 88 96 / 78 97 / 86	0.021 0.021 0.021

Table 3: *Summary of results obtained for waste-to-energy plants.*

The set of measurements made for the Milan Silla 2 plant results in concentration levels not particularly influenced by the ectent of dilution, with more or less constant average values of approx 11000 cm^{-3} for medium-low ratios of dilution ratios (RD = 15-35) and a slight increase, up to 17000 cm^{-3}, for higher dilutions (RD = 40-55). The hot gas test gave a concentration level of approx. 5000 cm^{-3}, slightly lower than the average levels found in the dilution tests, and, as already found for heating plants, confirms the formation of particles of condensable origin as a result of dilution and cooling; the observed increases, in terms of the ratio between the relative concentrations, vary between approx. two-fold for low dilutions (RD = 15-20) and 3.5 times for higher ones (RD = 40-55). Despite this, the average concentrations appear to be lower than those measured in the combustion air, which had a concentration of approx. 32000 cm^{-3}; this result is particularly important, especially when compared with those for domestic pellet and oil-fuelled boilers, which in this respect give quite opposite results. The size distributions shows fractions of ultrafine particles of 95% - 97%, not varying particularly with dilution ratios or hot gas tests; the number of nanoparticles seems relatively high, with fractions of between approx 79% and 93% going from low to high dilution ratios, and of 74% in the hot test. The distributions are generally characterized by a mode located in the nanoparticle range, although there are situations of bimodality with the presence of a second, coarser mode. The variations seem to be attributable to the extreme sensitivity of the mode characteristics of the distributions with respect to even very small fluctuations in the characteristics of the gases emitted, typical of the working conditions of full-scale plant fuelled by relatively heterogeneous waste matter.

The measurements at Brescia plant confirm levels of concentration which do not depend significantly on the dilution ratio applied. Average values are between approx. 4000 cm^{-3} for low and medium dilution ratios (RD = 15-35) and 7000 cm^{-3} for higher

dilutions. Analyses of combustion air indicate average concentrations of approx. 13500 cm^{-3}, which, being higher than those measured for plant emissions, confirm the similar and significant results found for the Silla2 plant. Size distributions are again heavily influenced by the presence of ultrafine particulate fractions, which make up over 90% of the total number, with no particular variation with dilution; the fraction of nanoparticles is again relatively large, between 71% for medium dilutions and 82% for higher dilutions. For the Brescia plant too, the distributions confirm the general presence of a main mode in the nanoparticle range, sometimes accompanied by one or more modes corresponding to coarser size fractions. As for the Milan plant, the changes found are here too due to distribution sensitivity with respect to variations in the gases emitted. The hot gas test, though carried out, did not produce any usable results due to some technical problems in the operation of the ELPI impactor, which made it impossible to measure concentrations.

The campaigns carried out on the Bologna plant gave average values generally higher than those for the other two plants, indicating a slightly increasing trend for progressively higher dilution ratios. Average concentrations shift from 46000 cm^{-3} for low dilution ratios (RD = 15-20) to 63000 cm^{-3} for medium ratios (RD = 25-35) up to 71000 cm^{-3} for the highest ratios (RD = 40-50). Hot gas tests measurements result in concentrations of approx. 25000 cm^{-3}, also slightly higher than data available for Milan plant; however, a comparison between cold dilution values from both plants shows the increase already observed for Milan plant, with ratios between corresponding concentrations of nearly 2 for lower dilutions and approx. 3 for higher dilutions, further confirming the formation of particles from condensable origin. Compared to values for combustion gas, which were on average approx. 20000 cm^{-3}, these results also indicate a detectable increase in the corresponding concentrations, not observed at the other two plants. Despite the complexity of the formation processes of the ultrafine fractions due to condensation, an important feature of the plant surveyed able to differentiate the results lies in the presence of a wet flue gas cleaning unit, which by causing even a limited increase in the humidity of the gases, could favor nucleation of residual matter present in the cleaned gas flow. Some evidence of this phenomena is reported in available experimental studies which highlight an appreciable tendency to the formation of ultrafine particulates in wet scrubbing systems, due to nucleation processes involving sulfur oxides. As regards size distribution, for the Bologna plant too the ultrafine particles prevail, with fractions greater than 95% both in tests with dilution and in hot tests; the nanoparticle fraction is always relatively large, increasing from 78% in the hot gas test to 88% in the higher dilution tests, in line with the increase found in the overall presence of condensable particulate. Size distributions in contrast are more uniform, generally with one mode in the nanoparticle range, at around 0.021 μm in both the tests with dilution and those on hot gas.

11.3 Capture efficiency of fabric filters

Measurements of the input flow to the filter, representing expected emission into the atmosphere without any removal treatment, results in total average particle concentration

of 7.6×10^{6} cm^{-3}, with a size distribution which in accordance with dilution conditions during sampling, is strongly characterized by the presence of ultrafine matter and nanoparticles from condensation. The corresponding measurements of outlet filter stream reveal average concentrations equal to 2.4×10^{5} cm^{-3}, more than ten times lower than those measured at input and with an almost identical size distribution; this means the filter removes ultrafine and nanoparticulate (20-100 nm) with an average efficiency of 97%, with a corresponding value for the submicron fraction (100-1000 nm) in the 98 – 99.9% range (Figure 9). A fabric filter is thus confirmed as a powerful capture system even for the ultrafine fractions either of primary origin (filterable fraction) than deriving from oth nucleation, condensation and coagulation effects arising from cooling and dilution of the flue gas (condensable fractions).

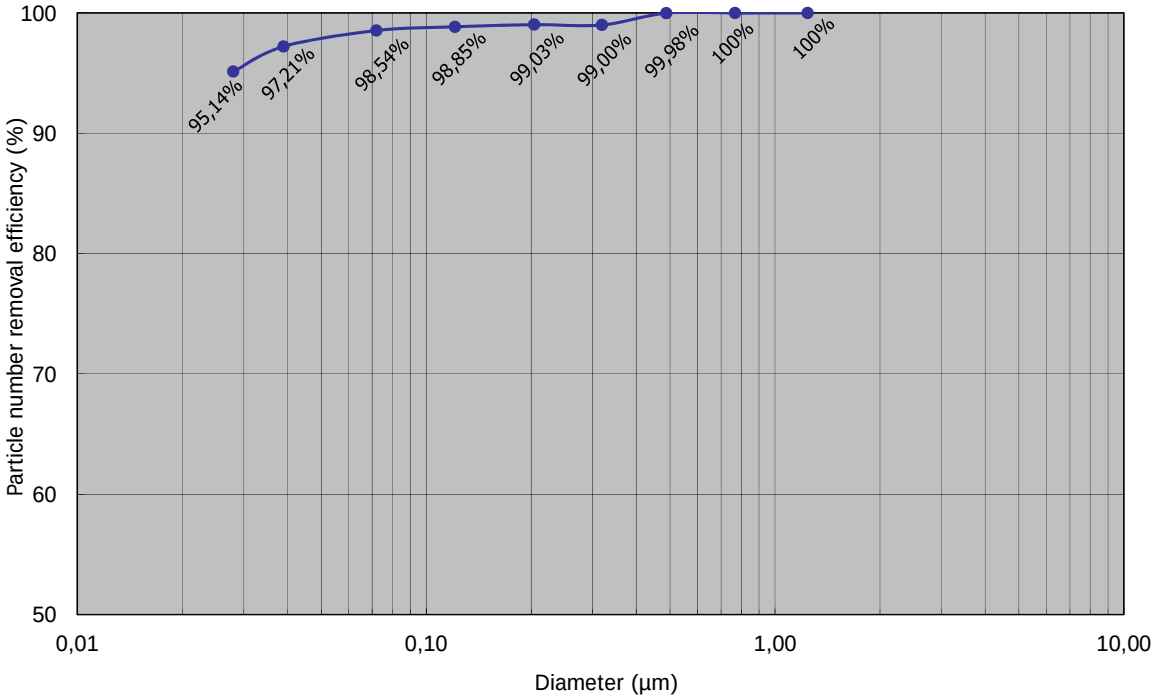


Figure 9: *Size-fractionated potential removal efficiency of fabric filter as measured during the investigation.*

11.4 Chemical characterization of UP from waste-to-energy plants

The composition of the nanoparticulate and ultrafine component obtained in the investigation is shown in Figure 10, where each slice of the pie represents the percentage of the component identified. The composition reflects fuel characteristics and the events of the combustion process type, with the presence of chlorides and metals, particularly zinc, iron and chromium, in accordance with the typical components of waste used feed to WTE plants.

From a comparison with the composition of the particulate present in the ambient air, in this case sampled at a site typical of urban area of Milan (Figure 11), the overall emission of ultrafine particles (> 100 nm) from the incinerator is richer in metals, especially iron, zinc, chromium and nickel and chlorides; the content of carbonaceous and ammonium component is lower, whilst that of nitrates is rather similar and sulfates are practically absent.

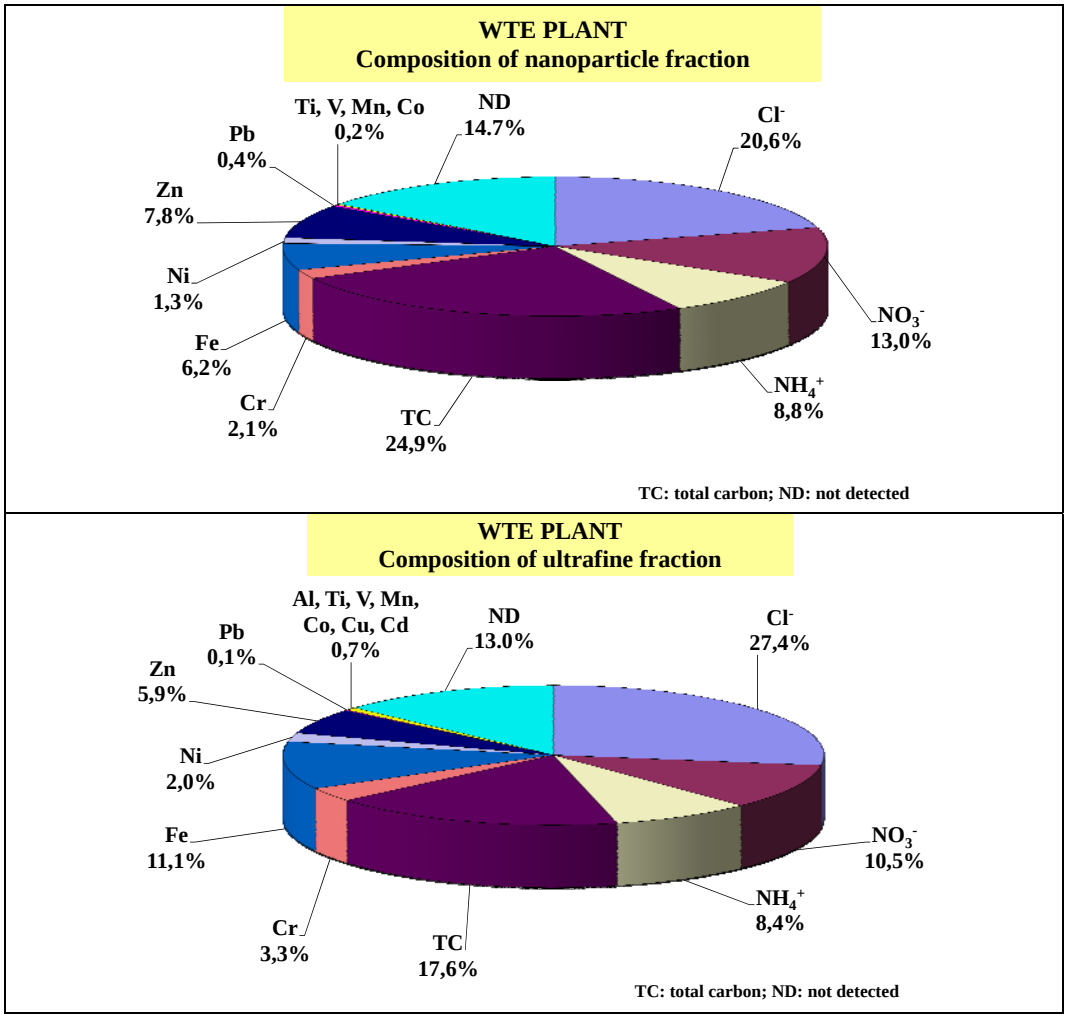


Figure 10*: Average composition of the nanoparticulate and ultrafine fractions emitted by a waste-to-energy incinerator*

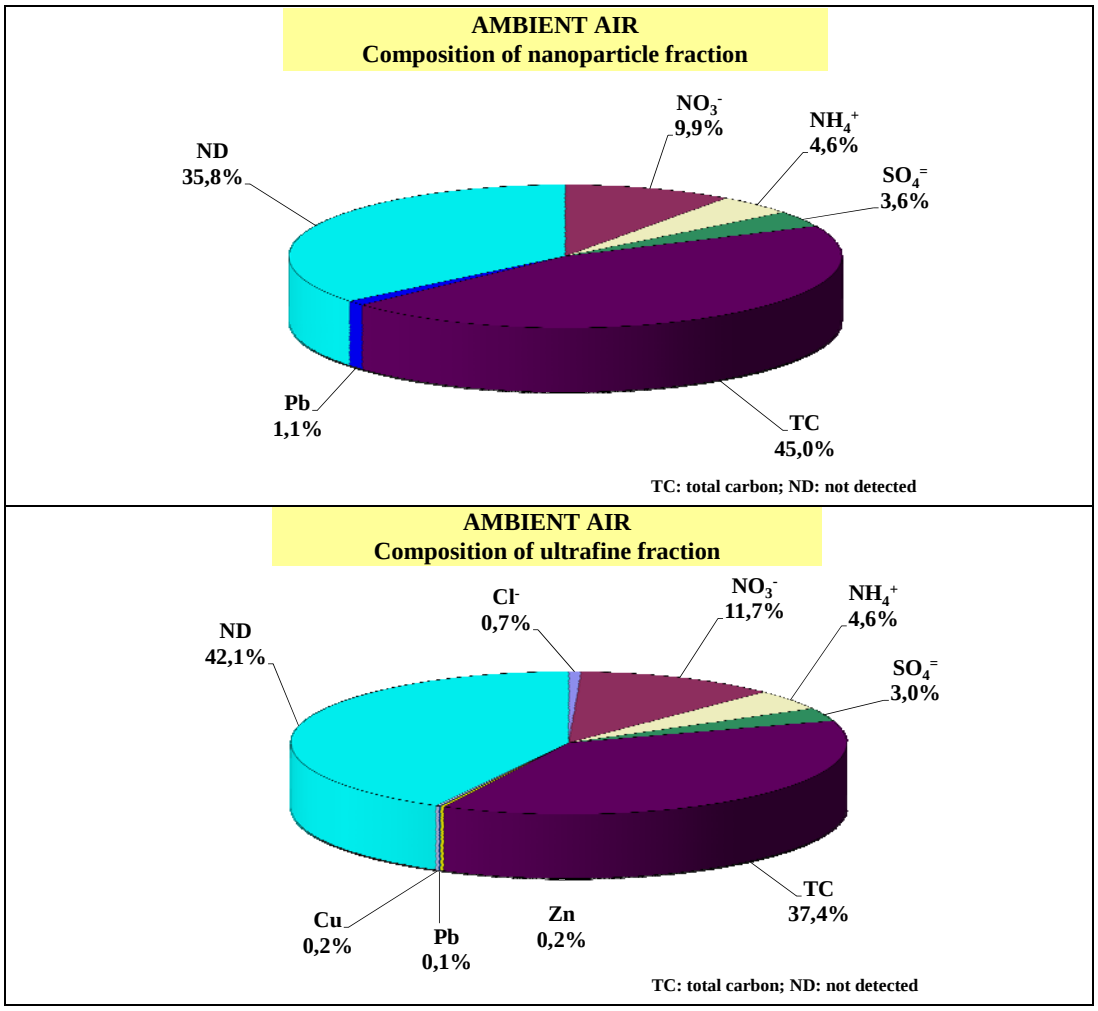


Figure 11*: Average composition of the nanoparticulate and ultrafine fractions in ambient air.*

11.5 Emissions from mobile sources

Given the extensive literature and the relative abundance of experimental data on UP and NP from automotive engines, during this study specific measurement campaigns were not carried out on mobile sources. The extensive bibliographic analysis revealed the situation summarized in Figures 12 and 13. Notwithstanding the poor repeatability and reproducibility of measurements of NP for engines running at variable regimes and loads over time, the analysis highlights the following considerations.

11.5.1 Diesel engines

Compared to a direct injection diesel engine with no kind of emission reduction device, the use of only a diesel oxidation catalyst (DOC) leads to a reduction by almost ten times in the number of NP and UP. The benefit is even greater if the DOC is coupled with a (cooled) exhaust gas recirculation (EGR) system.

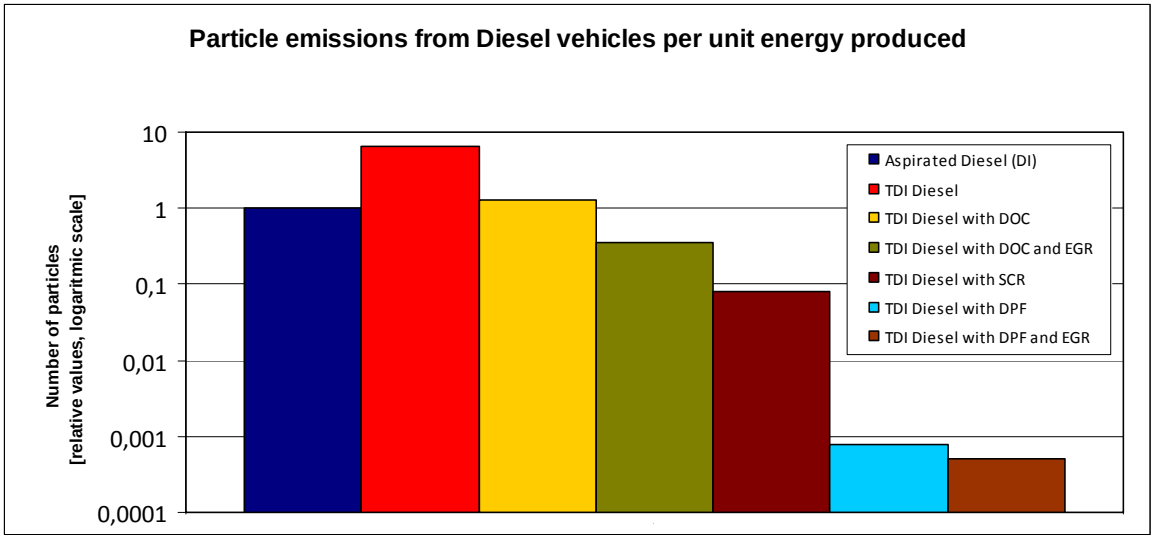


Figure 12*: Diesel engines – comparison between pollutant emission reduction technologies. The emissions measured were normalized compared to the emissions from a typical naturally-aspirated direct injection (DI) diesel engine, which fall within the range of 2-5 million particles per gram of fuel.*

Tests on heavy vehicles complying with Euro V regulations have shown that at high loads, the number of NP and UP after a Selective Catalytic Reduction (SCR) catalyst for nitrogen oxides is ten times lower than before the catalyst. At very low loads the difference is undetectable.

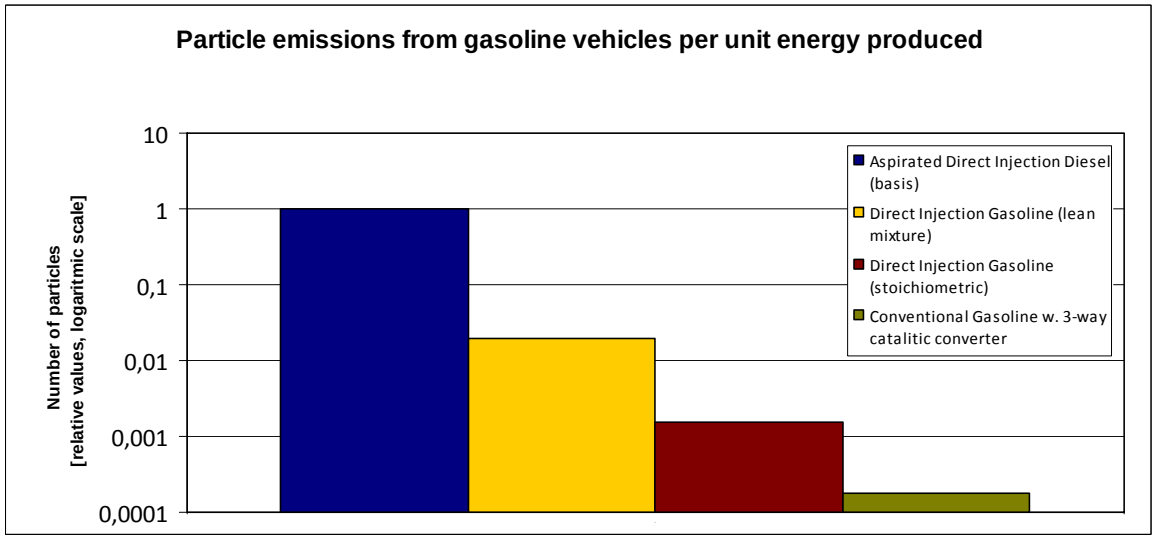


Figure 13*: Gasoline/Petrol engines – comparison between different engine technologies. The emissions measured were normalized compared to the emissions from a typical naturally-aspirated direct injection (DI) diesel engine, which fall within the range of 2-5 million particles per gram of fuel.*

However, by far the most effective device for the removal of NP and UP is the Diesel Particulate Filter (DPF), which reduces the total number of particles by about three orders of magnitude; a DFP is extremely efficient in retaining solid accumulation particles, while as reported above, the volatile nucleation particles tend to increase after the filter because of the reduction in the number of larger particles on which the volatile particles would otherwise condense.

11.5.2 Gasoline/petrol engines

Traditional Otto cycle indirect injection (MPI – Multi Port Injection) gasoline engines fitted with a three-way catalyst emit a number of particles comparable with the latest diesel engines fitted with DPF and cooled EGR. Data from the literature show instead that gasoline direct injection (GDI) engines fitted with a catalyst emit a higher number of NP and UP. Specifically, GDI engines operating at homogeneous load in stoichiometric conditions emit approx. ten times more NP and UP, while those operating with a stratified load and generally lean mixture emit a number of NP and UP which is two orders of magnitude greater than that measured for an indirect injection engine.

12 CONCLUDING REMARKS

Together with a number of natural sources, combustion is one of the several human activities whose emissions contain ultrafine particulate. With respect to stationary combustion sources, the main factors determining the emission of UP are related principally to fuel quality (from wood, with significant emissions, down to gas, for which values are lowest) and to the presence of fine particulate removal equipment, where particularly fabric filters have demonstrated excellent capture potential for UP too. However, there is actually no demonstrated evidence of a connection between specific stationary combustion activities, the presence of airborne ultrafine particulate and effects generated by the exposure to UP of specific groups of people. As for mobile combustion, vehicular traffic can be identified as a significant source, in the sense that near heavy traffic flows higher values of UP are found compared with urban background. Current efforts to control fine particulates are yielding appreciable results also in the reduction of the total number of particles emitted by diesel engines.

The main findings from the experimental research , summarized in graphical form in Figures 14 and 15, might be outlined as follows:

- ultrafine particulate (UP) emissions, i.e. particles included within the 0.007 – 0.1 μm size range, depend mainly on fuel quality, combustion process technologies and the presence and configuration of flue gas treatment systems;
- number concentrations measured for wood combustion in domestic heating plants are in the order of 10^7-10^8 cm^{-3}, 3 – 4 orders of magnitude higher than those found in

ambient air, without any appreciable difference between pellet boilers and closed fireplaces;

- concentrations by number measured for a fuel oil boiler are in the order of 10^6-10^8 cm^{-3}, comparable with those for wood;
- concentrations by number measured for the combustion of natural gas (4.5×10^3 cm^{-3}) are similar to, when not appreciably lower, than those found in ambient air;
- concentrations of UP measured at emission from WTE plants are generally at the same levels, when not lower, than those in the ambient air of plant site. The only exception is found for a plant equipped with a wet flue gas treatment unit, where the slight increase seems to be attributable to the corresponding small increase in the humidity content of the gas flow. For all plants studied, the concentrations measured are consistently lower by at least two orders of magnitude compared with those found for wood and oil combustion in domestic boilers, and only slightly higher than those produced by natural gas boilers;
- similar conclusions can be derived from emission factors calculated by resulting measurements and evaluated in terms of number of particles per mass unit of fuel used, given in Figure 13. Expected values for waste-to-energy plants are located on a range of levels aligned with, when not lower than, those typical of catalyzed gasoline vehicles and diesel vehicles equipped with DPF;
- both in domestic heating and in waste-to-energy plants, the condensable component has a significant effect in increasing UP emission levels;
- size distributions by number are characterized by the prevalence of ultrafine and nanoparticles fractions for all the plants studied;

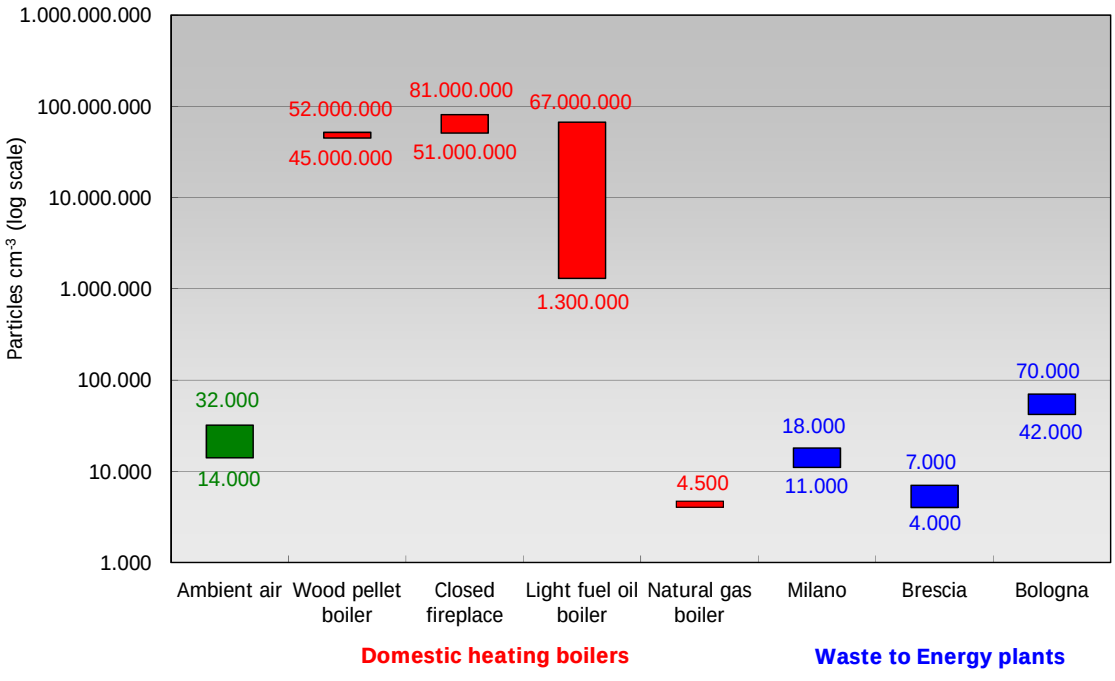


Figure 14: *Summary of the results obtained in the study*

- fabric filter confirms its recognized excellent potential for particle capture even in the ultrafine size range, with capacities for control both primary particles already present in the gas flow than those of condensable origin, arising from nucleation, condensation and coagulation process due to cooling and dilution of flue gases immediately after their stack emission into the atmosphere;
- the chemical composition of the nanoparticulate and ultrafine fractions emitted by urban-waste-to-energy plant is essentially in accordance with fuel characteristics and combustion process, with the presence of chlorides and metals, particularly zinc, iron and chromium, in line with the typical contents of the waste feed to WTE installation.

Therefore, the overall results arising from the study show how the activity of WTE plants, like all forms of combustion, contributes to the emission of UP, while to date there is no scientific evidence, either demonstrated or suspected, such as to rule out *a priori* this technique of waste disposal and energy recovery as a particularly significant source of nanoparticles. Regarding exposure and health risks, while due attention to the environmental role of ultrafine particulate and its components is necessary, analysis of epidemiological and toxicological implications in studies in this field yields no indications of particular risk attributable to UP deriving from waste combustion, provided plant is equipped and operated in accordance with the best technologies available in the field.

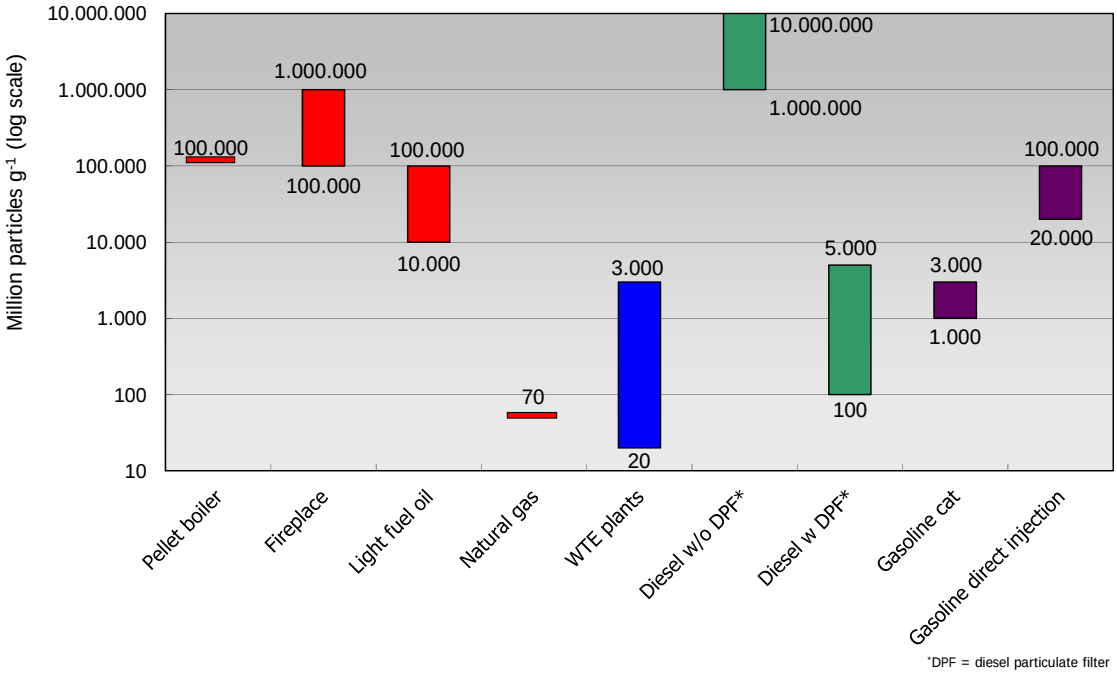


Figure 15: *UP emission factors for boilers and waste-to-energy plant (millions of particles per g. of fuel) estimated from the results of the experimental investigation, compared with typical values for light duty vehicles with diesel and gasoline engines.*