

Nanoparticles in the atmosphere

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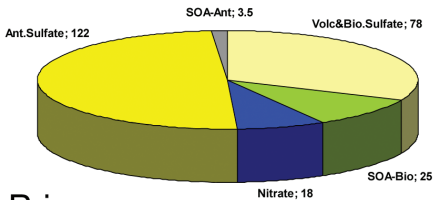
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1. Atmospheric particles and nanoparticles

Atmospheric particulate matter (PM) is a heterogeneous solid and/or liquid material (with the exception of pure water) present in a suspension into the atmosphere. The origin of PM can be natural or anthropogenic and may be primary, when emitted such as PM into the atmosphere, or secondary, when formed in the atmosphere from gaseous precursors. The term atmospheric aerosol is also used to identify PM, but in this case the gaseous matrix is also included.

As shown in *Figure 1*, at the Earth's scale most of PM has a natural-primary origin (97%), whereas the natural-secondary, anthropogenic-primary and anthropogenic secondary contributions are around 1% each. This means that on a global scale human activity mostly influences the secondary PM flux, since 56% of the global secondary PM has an anthropogenic origin (*Gieré and Querol, 2010*).

Secondary



Primary

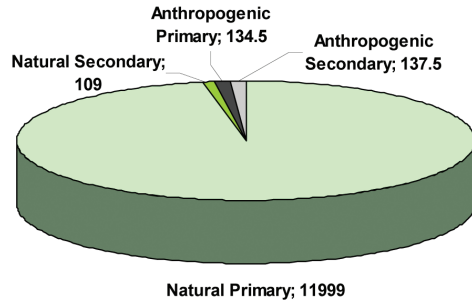
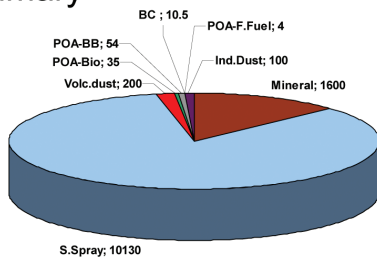


figure 1. Fluxes of primary and secondary atmospheric PM, expressed in teragrams per year ($Tg = 10^{12} g = 1 Mt$). Data represent "best guess" values of *Andreae and Rosenfeld (2008)*, except for volcanic particulate data, which are from *Durant et al. (2010)*. POA, primary organic aerosol; SOA, secondary organic aerosol; BC, black carbon; BB, biomass burning; F.Fuel, fossil fuel; Bio, biogenic; Ind, industrial; S.Spray, sea spray; Volc, volcanic; Ant, anthropogenic.

These relative contributions drastically change when we consider the source apportionment of PM at urban or industrial sites, where the anthropogenic load to PM prevails over the natural one and the secondary origin over the primary origin. As shown in *Figure 2*, particulate matter from anthropogenic sources constitute most of PM in the urban background of Barcelona, Spain (*Amato et al., 2009a*).

In atmospheric sciences the terms TSP, PM₁₀, PM_{2.5} and PM₁ are conventionally used for

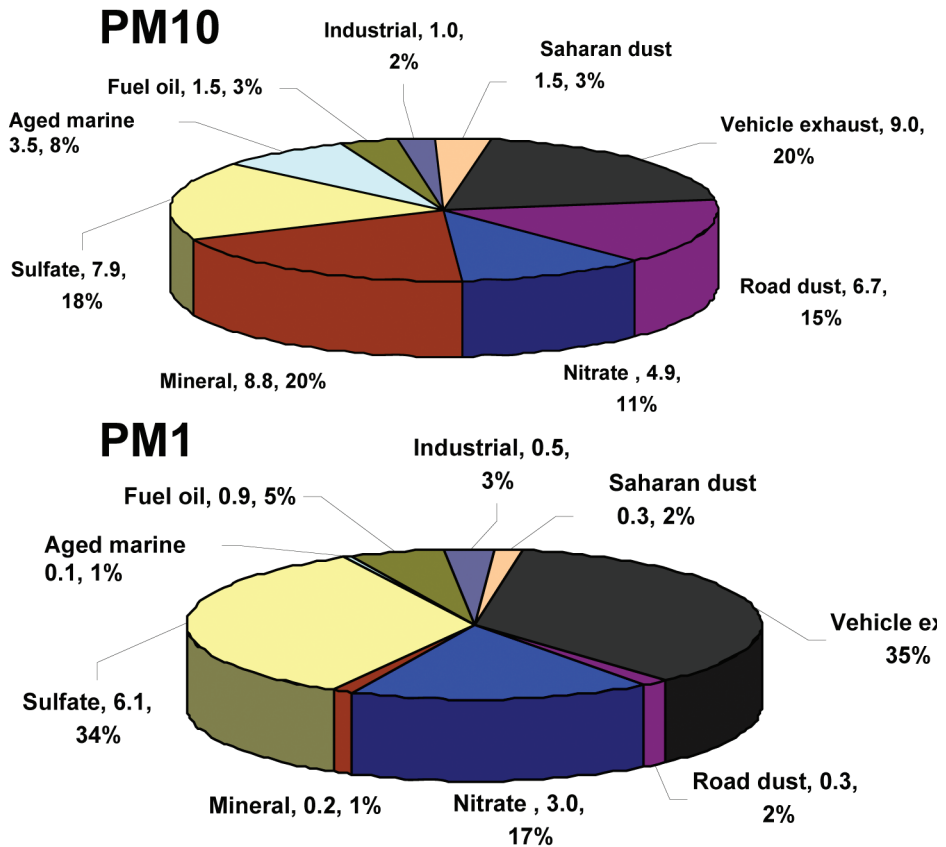


figure 2. Results from source receptor modelling showing source apportionment of PM10 and PM1 in urban background at Barcelona, Spain (Amato et al., 2009a).

the mass concentration of PM with aerodynamic diameters lower than 25, 10, 2.5 and 1 µm, respectively (Figure 3).

The term nanoparticles is not commonly used in atmospheric aerosol sciences, but the terms nucleation, Aitken and accumulation modes are employed to designate different particle sizes in the submicron range (Figure 3). Although nanoparticles may be considered as those particles in the submicron size range (i.e. <1000 nm, or submicron particles), a number of studies refers to nanoparticle when the size of the particle is <50 nm, including the nucleation mode (<30 nm) and part of the Aitken mode (20-100 nm). However, other studies use ultrafine particles (UFP, <100 nm) and nanoparticles as

synonymous. In a recent review, Kumar et al. (2010) consider nanoparticles equivalent to the size range <300 nm, given that 99 % of the ambient atmospheric particle number concentration falls in this size range. We will follow the same terminology in the present paper.

According the size partitioning and atmospheric aerosol processes the following features are reported for the size modes (Seinfeld and Pandis, 1998, Figure 3):

Ultrafine (100 nm)

The UFPs account for 80% of total number particle number concentration and these may be generated by nucleation from precursor

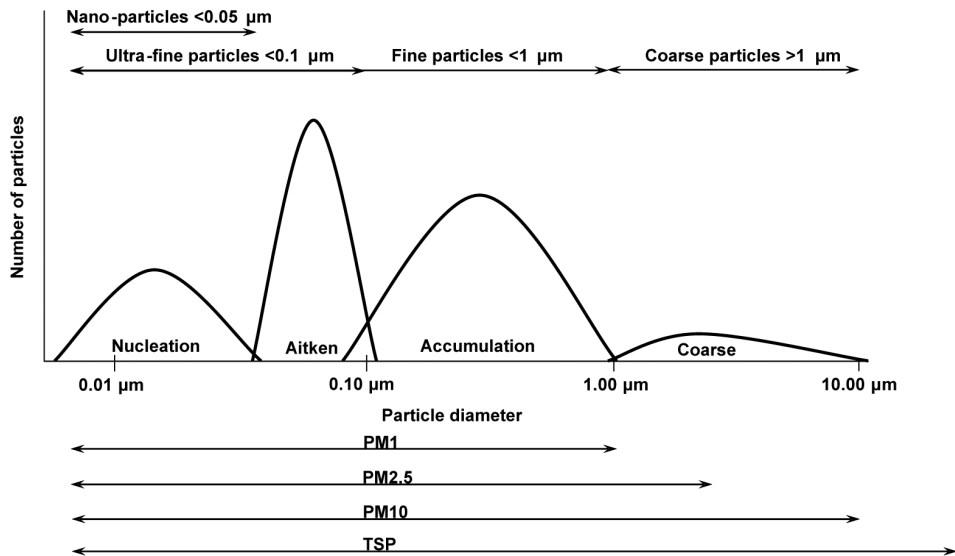


figure 3. Idealized size distribution of atmospheric aerosols, expressed in number of particles, modified from Warneck (1988) and Harrison and van Grieken (1998).

gases (secondary particles) or by direct emission as primary particles. Residence lifetime of UFPs in the atmosphere is very short (hours to 2-4 days). These particles are removed from the atmosphere by deposition (brownian diffusion), volatilization and by coagulation and condensation processes. These particles are found in high concentrations near the emission sources (Morawska et al., 1998). The size distribution changes rapidly with the distance from the emission sources as nucleation mode particles (<20 or 30 nm) grow fast by coagulation and condensation processes forming Aitken (20-100nm) and accumulation (100-1000 nm) mode particles (Charron and Harrison, 2003; Zhu et al. 2002).

Accumulation mode (100-1000 nm)

Particles in the accumulation mode contribute to 10-20% of the number of particles lower than 10 μm . However, this mode accounts for 40-70% of the mass of PM10. This mode is also characterized by the higher surface area of particles. These particles in the accumulation mode are mainly secondary formed by coagulation and condensation processes. Coagulation between finer particles is produced by Brownian motion and diffusion. This

process results in the reduction of the number of particles and in the growth of particle size and mass. Particles may act as condensation nuclei whereby gaseous species with low vapor pressure may condense. The condensation or adsorption of gas-phases onto pre-existing particles results in size growth and mass increase. Both coagulation and condensation processes are favored by high concentrations of particles. Particles in the accumulation mode present the longer residence time (> two weeks). These particles are mainly removed from the atmosphere by precipitation (in cloud and below cloud processes).

Coarse mode (1-10 μm)

Coarse particles are mainly primary, generated by mechanical processes from a variety of natural and anthropogenic sources, although coarse secondary particles may be formed by condensation/reaction of gases onto the pre-existing coarse primary particles. Contribution of these particles to the number of particles is very low (<<1%). The residence life time is very short and decreases with increasing diameter (hours for particles >20 μm and 2-4 days for particles with diameter of 2-3 μm , Meszaros, 1999), being

rapidly removed from the atmosphere by sedimentation processes.

The chemical composition of atmospheric particles varies widely with time, space and size of particles, but the following components are usually used to describe the aerosol speciation (term used in this field as synonymous of chemical composition) (*Gieré and Querol, 2010*):

- Secondary Inorganic Compounds (SIC). These are salts, mainly of NO_3^- and SO_4^{2-} with NH_4^+ , originated in the atmosphere from gaseous precursors, such as anthropogenic SO_2 , NO_x and NH_3 . The size of SIC is usually confined to <500 nm, with a mode in the accumulation size range. It is worth mentioning that sulphuric acid in relatively clean atmospheres nucleates from gaseous SO_2 , giving particles of diameter <20 nm that subsequently tend to grow up to the accumulation mode. Salts of some other cations (Ca^{2+} , Na^+ , Mg^{2+} ,.....) are also generally present, but in the coarse mode (>1000 nm), as a consequence of the interaction of gaseous precursors with mineral matter or sea spray.

- Sea Spray (SS) or marine aerosols. Chloride, Na^+ , SO_4^{2-} (the latter mainly from primary sea aerosol emissions, but also from the oxidation of marine biogenic dimethyl sulfide) and Mg^{2+} are, in decreasing order, the major SS components. Losses of Cl^- occur very often in aged SS as a consequence of the interaction of nitric acid with sodium chloride. The SS mostly contributes to the mass of the coarse mode.

- Mineral Matter (MM). Atmospheric dust arises from soil resuspension (natural or anthropogenic wind blown dust), demolition and construction works, industrial emissions, the abrasion of pavement and vehicle brake pads (*Amato et al., 2009b*). Accordingly with the differences in origin, its composition may vary a lot, but in most cases this mineral cocktail gives yield to a crustal composition, with Si, Ca, Al, Fe, K, Mg,, present in decreasing concentrations. As for SS, MM is also mostly contributing to the coarse mode of the aerosols.

- Bio-aerosols. These are particles with biological origin comprised mostly of organic carbon (OC). Bio-aerosols may be primary

(pollen, vegetal and insect debris, bacteria, spores, virus, humic substances) or secondary (organic aerosols formed in the atmosphere from reactive organic gaseous compounds, such as monoterpene and isoprene emitted by superior plants). Biological particles may vary widely in size, from the coarse mode of most pollen and debris particles to the very fine mode of secondary organic compounds formed by oxidation of gaseous biogenic precursors in forested areas.

- Carbonaceous anthropogenic aerosols are made up of OC and elemental carbon (EC). The later is supplied by graphitized carbonaceous particles arising from inefficient combustion of fossil and biogenic fuels (*Jimenez et al., 2009*). OC is more abundant (OC/EC varies from 2 to 15) and it is dominated by secondary OC (SOC) from road traffic, industrial, power generation and domestic and residential emissions, but also from biomass burning from domestic, agricultural and wild fires. An important proportion of SOC is water soluble. Primary OC is also present in aerosols due to the emission of combustion and non combustion sources, such as industrial emissions and tyre-asphalt abrasion. Specific compounds such as PAHs, alkanes, hopanes, steranes, waxes, sugars and cholesterol are used to trace the origin of carbonaceous aerosol mixture (including the biogenic ones). The grain size of OC and EC is relatively fine. Fresh soot particles from diesel engines reach median sizes of around 30-40 nm size.

- Trace elements. Aerosols may contain appreciable levels of a large number of trace elements associated with different natural and anthropogenic emissions. A number of minor and trace elements associated with the crustal load are usually present with a proportion >60% in the coarse mode (>1000 nm). For those elements related with the vehicle wear abrasion and high temperature processes this proportion decreases down to 40 and 20% respectively. Metals in the ultrafine size contribute very low to the mass load in aerosols but these may have a high relevance for health.

2. Origin of Nanoparticles

Most of the European population lives in

urban agglomerations. In these areas most of ambient air nanoparticles influencing human exposure arise from road traffic (exhaust) emissions. Locally, the influence of aircraft, shipping, industrial or construction works may be also of high relevance. In this paper the involuntarily man made nanoparticles are labeled as ultrafine particles (UFP). Furthermore, other types of man voluntarily made nanoparticles may have also relevance on a local scale. The latter are nanoparticles for industrial applications that may be emitted locally into the atmosphere (Kumar et al., 2010) during manufacturing or along the life cycle of manufactured products. Although the contribution of manufactured or engineered ones to the total nanoparticle concentration in ambient air may be negligible compared to other sources of particles, these may pose serious health risks (Andujar et al., 2009).

Ultrafine particles (UFP)

Here we include the inadvertent production of nanoparticles that may originate from both natural and anthropogenic sources, but which are mostly from the latter source in urban ambient air.

Urban UFP

The main traffic source of UFPs is diesel engines, both concerning mass and number concentration. Thus, a diesel engine emit from 2 to <20 times the mass and number concentration than an equivalent gasoline engine, although with specific driving conditions the proportion to total PM emissions (not the absolute value) of nanoparticles may be higher in gasoline vehicles (Kumar et al., 2010). A number of studies (Cheng et al., 2008; Holmén and Ayela, 2002) have demonstrated that cleaner fuels such as biofuels and gas clearly reduce the mass concentration of emitted particles, but not necessarily the number concentration. Probably old diesel engines emitted large mass concentrations of particles, but these were coarser and more reduced in number concentration. New combustion technologies, not only for automotive purposes, allow reducing the mass of the emission, but increase the number of nanoparticles. A step forward is made in Europe

with the new standard for PM from diesel vehicle exhaust, the EURO 6 standard, that fixes limit values in terms of both mass and number concentration.

In general, particles from vehicle exhaust can be divided into two broad categories, depending on the location of their formation. They can be formed in the engine or in the atmosphere after emission from the tailpipe (Shi and Harrison, 1999; Charron and Harrison, 2003). Particles formed within the engine are mostly submicrometric agglomerates of solid phase carbonaceous material ranging in size from 30 to 500 nm and residing mainly in the accumulation mode. Particles formed by condensation in the diluting exhaust plume are generally in the size range below 30 nm and are formed as the hot exhaust gases are expelled from the tailpipe of a vehicle, creating large numbers of very small particles in the air. The latter are semi-volatile and consist mainly of hydrocarbons and hydrated sulfuric acid (Shi et al., 2000; Caravaggio et al., 2007). The driving conditions influence the production of these semi-volatile nanoparticles and hence the shape of the particle size distributions, including the dilution rate, dilution ratio and temperature.

The finest nanoparticles, the so called nucleation particles with a size <20 nm, are scarcely emitted directly into the atmosphere, but generated in the atmosphere from inorganic and organic gaseous precursors, (such as VOCs, SO₂ and NH₃), by photochemical processes or when the emissions from combustion sources cool down (Kulmala et al., 2004). In order for nucleation to take place or to form new particles from gaseous species, relatively low levels of particulate and gaseous pollutants are required, since in high pollution conditions, condensation, causing growth of pre-existing particles, is favored instead of nucleation (Kulmala et al., 2004, Rodriguez et al., 2005).

The nucleation of H₂SO₄ + H₂O is thought to dominate in the free troposphere. But in the boundary layer (the lower atmospheric layer, where pollution is accumulated and convective dynamics prevail), it is known to be more complicated. The initial nucleation may also

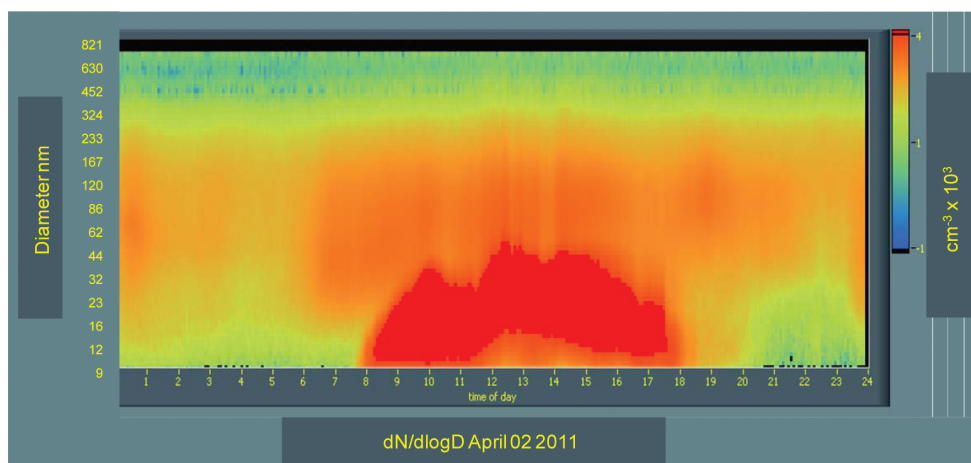


figure 4. Example of nucleation episode occurred on April 2, 2011 at Montseny (rural site, NE Spain). The nucleation episode observed occurred during an episode of Atlantic Advection, whereby air masses originating in the Western Atlantic brought clean, relatively unpolluted air to the MSY site. This was verified with low PM concentrations recorded for that day ($6.6 \mu\text{g m}^{-3}$ PM₁₀). Average temperatures for that day were 13°C with low relative humidity (52%). The lack of particles in the atmosphere (and thus, a lack of surfaces for gaseous precursors to condense upon), coupled with intense solar radiation measured on that day, allowed for nucleation processes to take place, as observed in the above figure. The nucleation processes began with the emergence of sunlight and increasing temperatures (8:00 am), and the continued throughout the day

be influenced by ammonia, amines, or organic molecules (Kulmala et al., 2004). The growth is often influenced or dominated by organic species, especially in forested sites, which are thought to be biogenic. Of all the biogenic species, terpenes and maybe sesquiterpenes are thought to participate in nucleation, while isoprene is thought to suppress it (Kjendler-Scharr et al., 2009). Figure 4 shows a nucleation burst episode followed by particle growth recorded in a rural background site at Montseny (Barcelona). According to the timing of the episode, sulfuric acid nucleation followed by growth caused by natural biogenic gaseous precursors from the surrounding forest is probably causing the nucleation burst in this case.

Typically in urban environments combustion particles are directly emitted from the exhaust mixed with a high concentration of volatile organic compounds (VOCs). With the dilution of the emission the external shell of particles is volatilized giving rise to very reactive gaseous species that will generate large amounts of particles in the atmosphere (Robinson et al., 2007 and Jimenez et al., 2009). Furthermore, the partial volatilization of the organic shell (mostly hydrocarbons) from these primary particles may give rise to nucleation-size particles (the non volatile

core). Dall'Osto et al. (2010) showed a remarkable shift in particle size distributions with major losses of the smallest particle class as particles are advected away from the traffic source, suggesting that nanoparticles are lost by evaporation, in addition to the coagulation processes.

In canyon and busy streets atmospheric nucleation processes are not frequently detected close to the kerbside. Although nucleation of particles may be produced only a few centimeters from the exhaust, these particles may grow very fast, and we consider these aerosol processes included into the emission and not as an atmospheric aerosol process, since this type of nucleation depends more on driving than atmospheric conditions (Wehner et al., 2009). As we leave the kerbside and we reach urban, sub-urban and rural background conditions, the atmosphere is becoming cleaner and nucleation of new particles may occur. These urban nucleation processes have special relevance in the Mediterranean region where insolation, dilution of pollutants by sea breezes and SO_2 emissions from shipping coincide in time, and favor photochemical nucleation (Figure 5, Pey et al., 2008, Pérez et al., 2010, Reche et al., 2011).

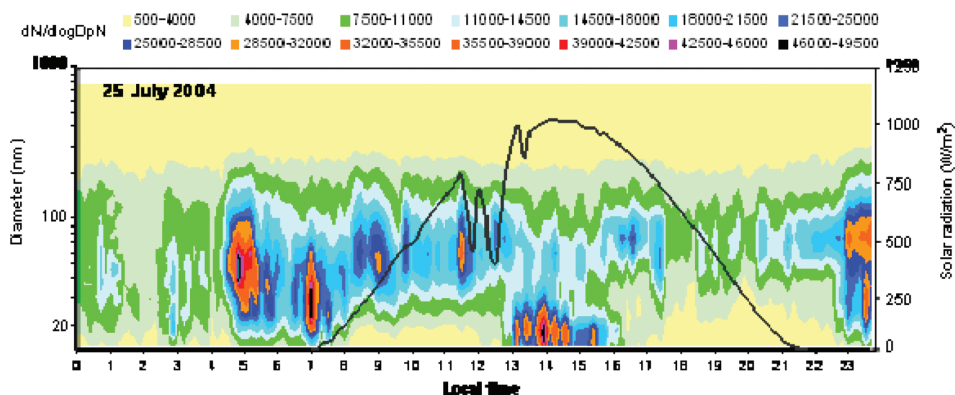


figure 5. Nucleation episode occurred in Barcelona in July 25, 2004. An intense burst of particles in the size below 20 nm occurred from 13 to 16 h local time, coinciding with the maximum in solar radiation.

According to the above processes and sources, the finest nanoparticles are made up of organic, sulfate and nitrate species. Very often nucleation is started by sulfuric acid and subsequently other organic (and probably inorganic) species condensate on the nuclei (Kulmala et al., 2004).

As previously stated, the **mid-sized nanoparticles**, from 20-100 nm, or Aitken particles, arise from the agglomeration of finer particles or by condensation on nucleation particles (Rodríguez et al., 2005), but in addition carbonaceous primary particles emitted directly from diesel engines are also relevant in this size range. The latter are known as 'soot' particles. These particles have a median size of 30-40 nm and are made up of an EC or ash core surrounded by a shell of organic species with inorganic impurities (Figure 6). These primary particles may dominate the particle number

concentration during traffic rush hours. As shown in Figure 7, the mean particle size for the maximum number concentration (known as DpN) peaks at around 35-40 nm during traffic rush hours in Barcelona, being an urban background site. Usually, the mid-sized nanoparticles are mainly made of organic material with sulfate and nitrate species (Kulmala et al., 2004).

The **coarser submicron particles**, those of the accumulation mode (100-1000nm) are also made of combustion (fossil and biomass burning) particles, but also of inorganic secondary species. Thus, the origin of these particles may be primary, but mostly secondary produced by coagulation of finer particles and condensation processes. The highest surface area (in cm^2/cm^3) is usually measured around 150-200 nm and consequently, in polluted environments, these high surface particles may act as

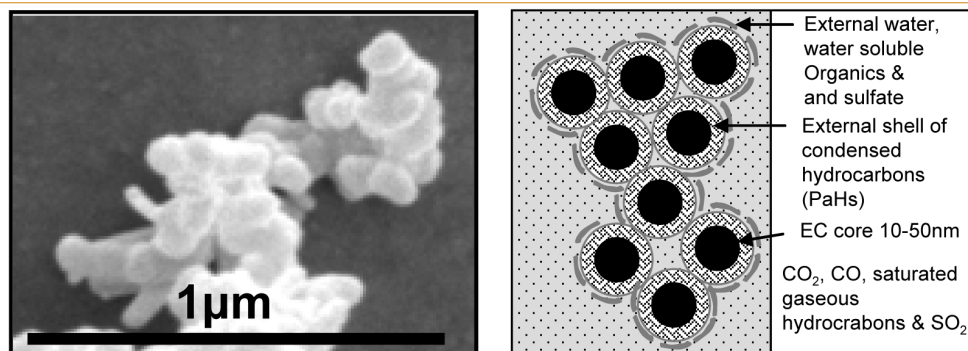


figure 6. SEM photomicrograph of diesel soot particles and their idealized structure and composition.

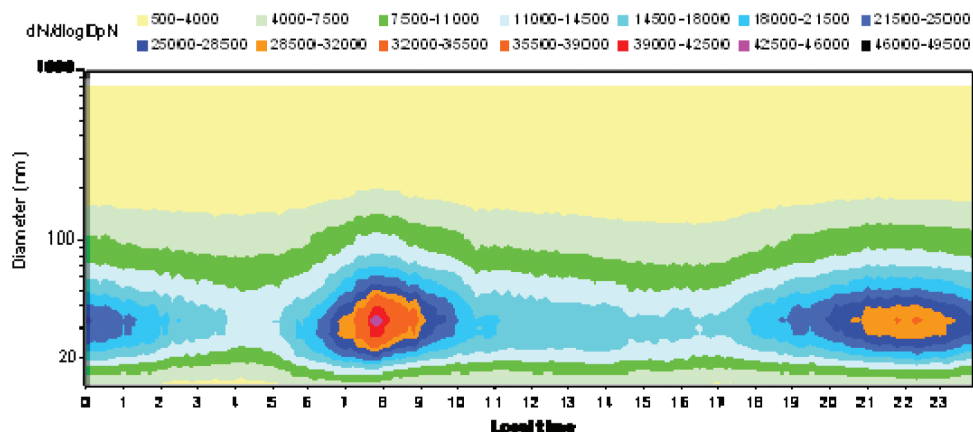


figure 7. Mean hourly levels of UFPs in Barcelona for the year 2004.

condensation nuclei for saturated gaseous organic and inorganic species.

In addition to the exhaust emissions, although in much reduced proportions, the wear processes originated between tyre and road pavement may contribute to increasing particle number concentrations. Studies indicate considerable nanoparticle emissions, depending on surface, vehicle and driving conditions. *Gustafsson et al. (2008)* and *Dahl et al., (2006)* carried out road simulator studies investigating physical and chemical properties of particles generated by the tyre-road interaction. The size distributions obtained revealed the unexpected production of UFPs when both studded and normal tyres were running on dense asphalt concrete (with granite stone material) and stone mastic asphalt (with quartzite). The broad maximum in the size distribution, typically around 15–50 nm (similarly to tail-pipe exhaust particles), did not change with type of pavement, but shifted towards smaller diameters when normal tyres were used and when the speed increased from 30–50 km h⁻¹ to 70 km h⁻¹.

These UFPs had very heterogeneous forms such as carbon chains, droplets and granules, and were therefore associated with an organic origin (*Gustafsson et al., 2008; Dahl et al., 2006*). It appears likely that the near-spherical particles and their agglomerates

originate from the carbon black reinforcing filler (such as black carbon). Another possibility is that the particles originate from small tyre inclusions of excess ZnO or ZnS. Zinc oxide is an activator for organic accelerators used to speed up the vulcanization process. Zinc sulfide is used as a vulcanizer in nearly all rubber products and is present in tires in concentrations of typically a few percent by weight (*Dahl et al., 2006*).

Demolition works may increase the ambient particle concentrations although studies on this subject are extremely scarce. According to *Hansen et al. (2008)* the concentration increase is size dependent, varying from a factor of 1.6 for the UFPs to 3.3 for the particles >1 µm.

Trace metals

Trace metals, although low in mass concentration, are ubiquitous in our urban atmospheric environments. For example, V, Ni, Co, Sb, Cr, Fe, Mn, Cu, Zn, As and Sn are emitted to the atmosphere by fossil hydrocarbon combustion and metallurgical industrial activity (e.g. *Pacyna, 1986; Querol et al., 2002; Moreno et al., 2008*), and traffic pollution involves a wide range of trace element emissions that include Ba, Pb, Cu, Cr, Sn, Sb and Zr (e.g. *Birmili et al., 2006; Amato et al., 2009b; Bukowiecki et al., 2010*). Atmospheric metalliferous particles tend to occur in the nanometric size range

(*Utsunomiya et al., 2004; Pérez et al., 2008*), which not only results in large surface areas being available for reaction with human fluids, but also makes them able to be transported over distances of hundreds of kilometers.

Any review on metaliferous nanoparticles reveals the relatively small number of studies focused on particle chemistry (*Morawska et al., 2008*), with most of literature being related to traffic emissions. Thus, examples of previous studies have identified trace metals in aerosols in Detroit as individual particles as small as 10 nm (*Tolocka et al., 2004*), or in Mexico City where 0.05 - 0.3 μm particles were demonstrated using TEM to be internally heterogeneous with concentrations of V, Cr, Mn, Ni, Zn, Sn, Pb, and Bi in 50% of the individual aerosols examined (*Adachi and Buseck, 2008*). Nanoparticles in Mexico City are also commonly rich in Pb, in many cases co-existing with Zn (*Salcedo et al., 2010*). At a traffic site in southern Taiwan nanoparticles were enriched in traffic-related metals (Pb, Cd, Cu, Zn, Ba, and Ni) compared to particles of other sizes (*Lin et al., 2005*). Nanoparticles rich in Ag, Ba, Cd, Pb, Sb, V, and Zn were strongly associated with diesel fuel, while Cu, Mn, and Sr were strongly associated with gasoline. In addition to the fuels and lubricating oils contributing to particle formation in engine exhausts, metal parts from engines and catalytic converters, including Pt, Pd and Rh, may also potentially be emitted as nanoparticles (*Biswas and Wu, 2005*).

Several manuscripts deal with open highway-related metals in nanoparticles. *Ntziachristos et al. (2007)*, for example, measured trace metals in the ultrafine and accumulation modes next to a busy Southern California freeway and showed that metals related to mechanical processes (road, wheels and brake abrasion) or derived from crustal materials were predominantly present in supermicron particles. Other metals showed similar concentrations across the lower size ranges and so display a more flat size distribution (Cu, Pb). In fact several of the potentially most toxic metals (e.g., Pb, Sn, Ni, Cr, V, Ba), many of them tracers of vehicular emissions from nearby freeways, have been described

as predominantly partitioned in the submicron particles within Los Angeles basin (*Singh et al., 2002*). It is clear from such work that PM released on the open highway significantly contributes to the emissions of Sb, Mo, Cu and Ba, and Sb, Cu and Ba in the PM_{0.18} and PM_{0.18-2.5} size ranges respectively.

Airports, harbours, and industry:

Aircraft operations increased the UFPs concentrations by factors of 10 and 2.5 over background levels at 100 and 660 m downwind, respectively (*Hu et al., 2009*); and by factors of 13-90 at a site 500 m downwind of the airport (*Westerdahl et al., 2008*). Spikes in UFPs concentration (up to $2.2 \times 10^6 \text{ cm}^{-3}$) were observed and associated with jet take-offs 100 m downwind of the takeoff area. These concentrations were around 440 times the background concentrations (*Hu et al., 2009*); Concentrations up to $4.8 \times 10^6 \text{ cm}^{-3}$ have also been measured (*Westerdahl et al., 2008*). Elevated UFPs concentrations were also associated with jet taxi and idle, and operations of propeller aircraft. The median mode of the UFPs associated with aircraft operations reported by the aforementioned studies had a median mode of about 10-15 nm (electric mobility diameter).

UFPs dominate particulate emissions from shipping (*Isakson et al., 2001; Cooper, 2003; Healy et al., 2009*). Studies on marine engines operating on biodiesel found particles in the accumulation mode with number electrical mobility mean diameters ranging from 63 to 82 nm at the ISO modes and from 89 to 99 nm at idle (*Jayaram et al., 2011*). UFP number concentrations in the range of 0.01-0.10 μm associated to ship plumes were 3 times higher with respect to urban background levels with a bimodal size distribution (*Isakson et al., 2001*). Conversely, the mass particle size distribution in the interval 0.01-0.63 μm was not significantly affected by the presence of ship plumes (increased by a factor of 1.3, *Isakson et al., 2001*).

The strong influence of industrial emissions on the presence of nanoparticles in the atmosphere is also documented, although in

most analyses such nanoparticles are a mixture of both industrial and traffic emissions. Steelworks were found to emit PAHs mainly in the ultrafine fraction (Baraniecka *et al.*, 2010). The coal-fired power plants are one of the major anthropogenic sources of UFPs. Liu *et al.* (2010) found that UFP emissions from boilers with low NO_x burners (LNBs) were higher than those from boilers without LNBs. Yi *et al.* (2008) found that the number size distributions of particles (0.03-10 µm) emitted from several coal-fired power plants in China displayed a bimodal distribution. Other studies in a lignite-fired power plant in China found a clear peak at 10 nm (Wang *et al.*, 2008). Linak *et al.* (2007) found that coal ultrafine ash may contain significant amounts of carbon, and some chromium and thiophenic sulphur. UFP concentrations near a coal fired power station were believed to have been derived from precursor emissions from the power stations, although no primary particulate material was observed in the <0.3 µm fraction (Hinkley *et al.*, 2008).

Engineered nanoparticles

Engineered nanoparticles are manufactured to have specific properties or composition, and are considered distinct from air pollution nanoparticles based on the fact that these are not purposely produced.

From a chemical point of view, engineered nanoparticles are typically mineral (e.g., TiO₂; quantum dots), metallic (Fe₃O₄; nanowires) or carbon-based (carbon nanotubes; fullerenes). According to the British Standards Institution (BSI, 2007), engineered nanomaterials may be classified into four hazard type groups:

1. **Fibrous nanomaterials**; insoluble particles with length to diameter ratio of >3:1 (Donaldson *et al.*, 2006). The most common nanomaterials in this group are carbon nanotubes and nanowires.

1.1. **Carbon nanotubes (CNTs)**: attractive for commercial application due to the fact that they are around 100 times stronger than steel, CNTs are only a fraction of the weight.

1.2. **Nanowires**: electrically conducting or semi-conducting nanofibres, which can consist of carbon, metals, oxides, sulphides

or nitrides. Examples of nanowires are zinc oxide (ZnO) nanowires, with semiconducting nature and unique optical and piezoelectric properties.

2. **Nanomaterials classified as carcinogenic, mutagenic, asthmagenic or reproductive toxins** (CMAR). Examples of CMAR nanomaterials are nickel, arsenic and cadmium nanoparticles.

3. **Insoluble nanomaterials**: insoluble or poorly soluble nanomaterials not in the fibrous or CMAR category:

3.1. **Quantum dots (QDs)**: quantum dots, or nanocrystals, are semi-conductors which have unique optical properties making them useful in, among other purposes, diagnostic medical imaging. Quantum dot toxicity is dependent on the stability of the surface coating (Hardman, 2006; Powell, 2006).

3.2. **Fullerenes**: the most common form of fullerenes (Kroto *et al.*, 1985) is a hollow sphere which contains 60 carbon atoms. They have unique physical properties, as they retain their original shape after being exposed to extreme pressures. Fullerenes are hollow structured and can therefore be filled with different substances, which gives them potential for drug delivery.

3.3. **Titanium Dioxide (TiO₂)**: nanoscale TiO₂ has a wide range of applications, such as being used in paint and sunscreens.

3.4. **Soluble nanomaterials**: soluble nanomaterials are nanomaterials which do not belong in the fibrous or CMAR category and which are soluble. Most engineered nanomaterials have low solubility (Colvin, 2003).

Exposure to engineered nanoparticles occurs mainly in the workplace (e.g., from manufacturing processes), even though it may also take place in ambient air (from fugitive sources, with minimal contributions to ambient air nanoparticle levels). In the workplace, exposure can occur during synthesis, downstream use, application or treatment of products containing embedded manufactured nanoparticles, and waste recycling/disposal. Fugitive diffuse and point source emissions may occur during the various stages in the manufacturing process (Demou *et al.*, 2009; Park *et al.*, 2009). Finally, further processing may take place such as surface modification,

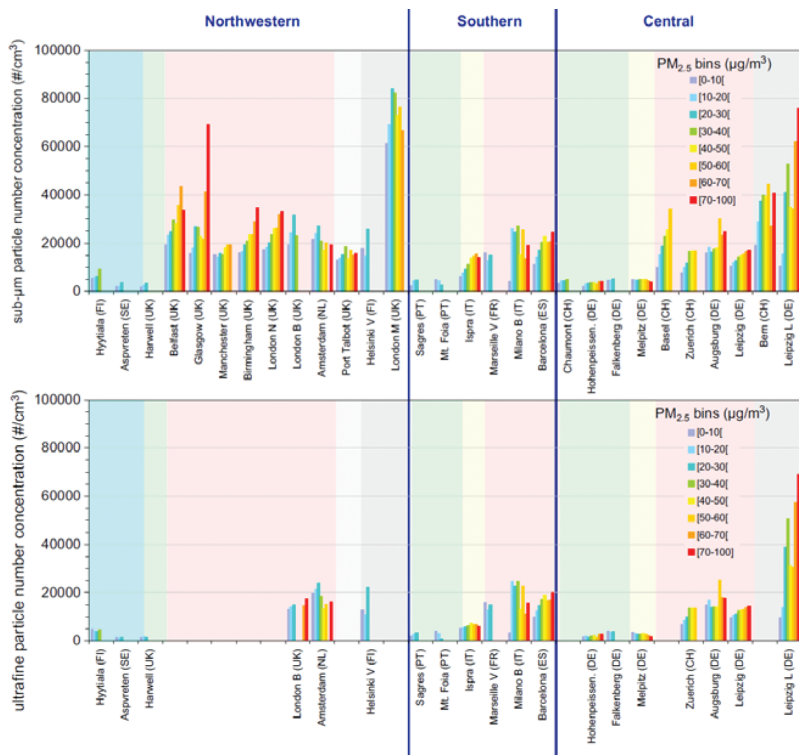


figure 8. Submicron (10-800 nm) and ultrafine (<100 nm) particle number concentration averaged over 10 µg m⁻³ PM_{2.5} bins at different sites of Europe, from Putaud et al. (2010). Pastel background colors indicate the site types (blue: natural background, green: rural background, yellow: near city, rose: urban background, light grey: industrial, grey: traffic kerbside).

before the product is transported to the downstream user. Generally, downstream users will mix or disperse the manufactured nanoparticles with other materials to form the end or intermediate product.

3. Levels of Nanoparticles

As shown by Figure 8, a recent European compilation of data on levels of submicron and ultrafine particles (Putaud et al., 2010) shows that in remote and rural areas mean annual particle number concentrations (between 10 and 800 nm) reach usually <500 and <1000 cm⁻³, respectively. Most of sub-urban and urban background sites record levels < 1.5 x 10⁴ and < 2 x 10⁴ cm⁻³, respectively, but traffic sites may increase annual mean values by a factor of 4 with respect urban background.

The Barcelona case study

Mean urban background annual number con-

centration of UFPs (5 to 800 nm) in Barcelona reaches around 1.5 x 10⁴ cm⁻³, in the range of most European cities. Levels of UFPs at Barcelona are mostly controlled by primary vehicular emissions, but other source contributions may be also found in relatively lower proportions. In order to ascertain these sources and their contribution, a receptor modelling analysis of the 2004 geochemical database of PM₁₀, PM_{2.5} and PM₁ was performed by Pey et al. (2009). This study identified seven sources, among which five (vehicular emissions, sea spray, mineral matter, fuel-oil combustion and industrial emissions) were identified as actual emission sources, being the other two atmospheric processes (photochemical nucleation and regional-urban background). After the identification of the sources, a regression analysis was done, allowing the daily quantification of contributions from each source or atmospheric processes. This was done both for the total number and for specific particles sizes. Vehicular emissions (exhaust emis-

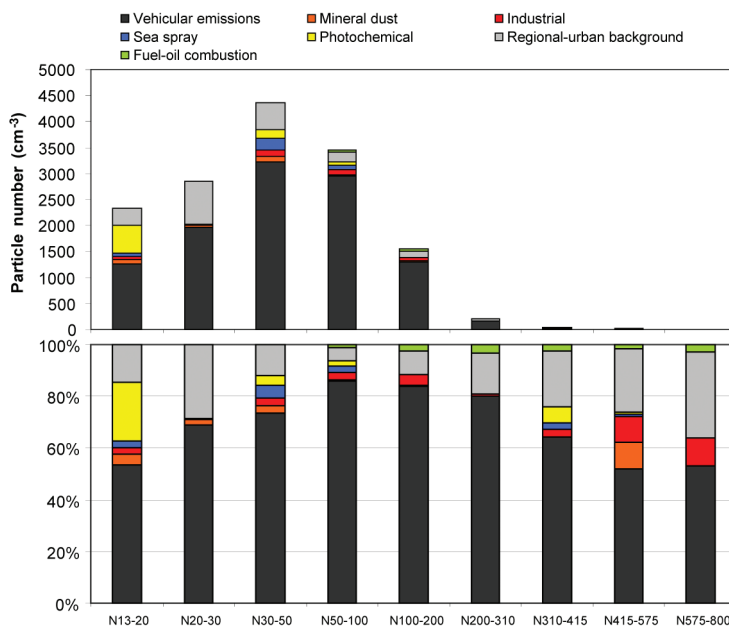


Figure 9. Mean 2004 source apportionment of particle number concentration of different size ranges between 13 and 800 nm in Barcelona. Modified from Pey et al. (2009).

sions) emerged as the major source of nanoparticles, accounting for almost 70% of them (Figure 9). These particles are dominating the number concentration between 30 and 300 nm, although they have their maximum in size distribution only between 30 and 100 nm (Figure 9). The second contributor to nanoparticles in the Barcelona atmosphere is the regional-urban background (also containing aged traffic derived particles) component, accounting for about 25% of them. These particles are significant in terms of number in the Aitken and accumulation mode. The other five sources accounted for less than 10% of the total number. The most important among these five is the photochemical nucleation (about 3% of the total number, Figure 9), essentially evident in the particle size between 10 and 20 nm. In this range the photochemical nucleation accounts for around 20%. Whereas vehicular emissions did not show seasonal patterns, the photochemical nucleation recorded a clear seasonal dependency, with a maximum prevalence in mid summer.

4. Health Effects of Nanoparticles

The diverse health effects caused by atmos-

pheric aerosols are due to the wide range of physical (size, surface, and morphology) and chemical (toxicity, acidity, oxidative stress, solubility) properties of aerosols. Although a number of studies demonstrated that the finer particles affect health, coarse particles have also impact on human mortality and morbidity. This is due to the fact that there are different components (with different composition and size) in atmospheric aerosols that may have health effects.

Comprehensive scientific literature reviews on health effects of nanoparticles have been provided by Biswas and Wu (2005) and Bystrzejewska-Piotrowska et al. (2009). Nanoparticles, independently of their toxicity, may overpass the alveoli in lung and cause cardiovascular problems, such as atherosclerosis (Künzli et al., 2011), may trespass the nasal respiratory epithelial barrier and reach the brain directly (Block and Calderón-Garcidueñas, 2009), or deposit in the alveoli (Oberdörster, 2001) decreasing the ability of alveolar macrophages to attack foreign particles which become overwhelmed by the vast number of incoming aerosols (Donaldson et al., 2001).

A major cause for concern related to exposure to nanomaterials is that there is evidence that particles in the nano-state are more toxic than their larger counterparts of the same material (Faux et al., 2003). An added concern is that the toxicity of nanomaterials may be altered by changes to the surface chemistry (Royal Society / Royal Academy of Engineering, 2004). Nanoparticles containing zinc, aluminum or copper oxides, fullerenes, or carbon nanotubes are indeed toxic to cells, and that complex interactions between particles and gaseous components can act synergistically to increase their toxic effects (Biswas and Wu, 2005 and references therein). In addition there is emerging evidence that some nanomaterials which have fibre-like dimensions show asbestos-like, length dependent pathogenic behaviour (Poland et al., 2008).

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