Chapter 23

Atmospheric Nanoparticles and Their Impacts on Public Health

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Additional information is available at the end of the chapter

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1. Introduction

The World Health Organization (WHO) estimates that every year around two million people die annually due to the effects of atmospheric pollution (Tranfield & Walker, 2012). These estimates are based on epidemiological studies that showed associations between air pollution exposure and respiratory and cardiovascular illnesses and deaths. Special efforts thus have been made in order to reduce air pollution on a global level (Slezakova et al., 2012) and, more importantly, aiming to reduce the adverse impacts of atmospheric pollutants. Although these efforts have been leading to a reduction of risks and effects, air pollution is still a matter of great concern, mainly to relative impacts on human health.

Air pollution is a mixture of various gases such as ozone, carbon monoxide, sulphur dioxide, and nitrogen dioxide combined with airborne particles in sizes range of few nanometers to hundreds of micrometers. According to the WHO, these particles are one of the most important pollutants of present times and their presence in the atmosphere has harmful effects both on human health and environment. Nanosized particles (i.e. smaller than 100 nm) are a subgroup of atmospheric particles. Though humans have been exposed to nanosized particles throughout their evolutionary stages, the respective exposure has dramatically increased over the last century due to contribution from various anthropogenic sources. In addition, the rapidly developing field of nanotechnology is likely to become another source of these particles through increased use of engineered nanomaterials. Thus information about safety and potential hazards is urgently needed. Apart from their role for possible adverse health effects (Hoek et al., 2010; Knol et al., 2009), nanoparticles are important precursors for the formation of coarser particles that are known to strongly influence global climate (Intergovernmental Panel on Climate Change [IPCC], 2007; Strawa et al., 2010) and urban visibility (Horvath, 1994). They may
also influence the atmospheric chemistry in general as their chemical composition and reactivity are different from coarser particles, thus opening novel chemical transformation pathways in the atmosphere (Anastasio & Martin, 2001).

This chapter focuses specifically on airborne nanosized particles and their importance to public health. Various aspects are discussed in the following sections including sources, levels, chemical compositions, regulations, and health and environmental impacts.

2. Characteristics of atmospheric particles

2.1. Particle sizes

The size of particles in the atmosphere ranges from few nanometers up to hundred micrometers. There is no doubt that the particle size is an important parameter. It controls much of the dynamic behavior of particles as well as their chemical and physical impacts upon the environment. It is also certainly an important parameter for the health consequences of the respective human exposure as particle size determines: (i) the deposition of particles within human respiratory system; (ii) the amount of surface area that can contact tissues; and (iii) the rate of particle clearance from lungs (Oberdörster et al., 2005). Particles have many irregular shapes so their aerodynamic behavior is expressed in terms of the diameter of an idealized sphere (i.e. aerodynamic diameter), which is usually simply referred to as “particle size”. Up to this date various terminologies in relation to particle size are used to describe atmospheric particles. Medical sciences use terms such as inhalable or respirable particles that derived from particles classification according to the entrance into various compartments of the respiratory system (WHO, 2000). Toxicologists typically describe particles as ultrafine, fine and coarse whereas regulatory agencies, namely WHO, US Environmental Protection Agency (USEPA) and European Union (EU) use terms such as PM\(_X\) where PM stands for particulate matter and the subscripts identifies the upper 50% cutpoint. The aerosol science uses classification of particles into the modes based on the particles diameter. Each mode has distinctive size range, formation mechanisms, sources, chemical composition and deposition pathways (Hinds, 1999).

Typically, the mass-based size distribution of atmospheric particles is bimodal, with a minimum point that generally occurs in the size range of 1000–3000 nm (i.e. 1–3 μm; Sioutas et al., 2005), which distinguishes the coarse and fine modes (Fig. 1). By convention, the coarse mode consists of particles larger than 2500 nm in aerodynamic diameter. Based on their size, the coarse mode particles can be further subdivided into supercoarse and coarse particles. The coarse particles have diameter between 2500 nm and 10000 nm (Fig. 1). These particles are usually produced by mechanical processes such wind erosion. Particles from sea salt sprays, pollen and spores also belong to this mode as do coarse particles from plant fibers and leaves. As coarse particles are large, they settle out of the atmosphere typically within few hours of formation. Coarse particles deposit in the upper airways of the human respiratory system and they are cleared from human body through nose or by coughing or swallowing. The super-
Coarse particles are those with aerodynamic diameter bigger than 10000 nm (i.e. 10 μm; USEPA, 2012a). As these particles are too large to enter human respiratory system they are not considered as relevant from the health point of view. However, due to their possible environmental impacts, supercoarse particles are partly assessed when evaluating total suspended particulate matter (TSP) which includes particles of size range up to 30000 nm (i.e. 30 μm).

Figure 1. Schematic representation of the size distribution of atmospheric particles.

Fine mode is composed of particles with aerodynamic diameter smaller than 2500 nm (Fig. 1). Typically, these particles are generated by anthropogenic sources. The small sizes of the particles make them less susceptible to the gravitational settling resulting in atmospheric lifetimes in range of days up to weeks and the ability to travel over very long distances in the atmosphere (Anastasio & Martin, 2001). When inhaled fine particles deposit in the conducting airways of the lungs but some of them can penetrate beyond conducting airways into the alveolar region. Based on the formation mechanisms fine mode particles are further subdivide into accumulation and nuclei modes. Accumulation mode consists of particles with aerodynamic diameter between 100-1000 nm. They result from anthropogenic sources (combustions of engine fuel and lubricant oil by diesel-fuelled or direct injection petrol-fuelled vehicles; Kumar et al., 2010, 2011) but can be formed by natural formations, i.e. by coagulation of nuclei-mode particles or by condensation of gas or vapor molecules on the surface of existing particles.
Coagulation is most efficient for large numbers of particles, and condensation is most efficient for large surface areas. Thus the efficiency of both coagulation and condensation decreases as the particle size increases which produces an upper limit of approximately 1000 nm beyond which particles do not grow by these processes. Particles in the range of 100-1000 nm are important because they can represent a significant fraction of the particulate emissions from some types of industrial processes. In addition, sizes of particles in accumulation mode are comparable with the wavelengths of visible light, and hence they account for much of the anthropogenic visibility impairment problem in many urban areas (Seinfeld & Pandis, 2006).

Nuclei mode consist of particles smaller than 100 nm that are also called as ultrafine particles or nanoparticles. In the atmosphere these particles are formed through nucleation, i.e. condensation of low-vapor-pressure substances formed by high temperature vaporization or by chemical reactions in the atmosphere to form new particles (nuclei). These particles are traditionally considered as fresh emissions that yet have to undergo chemical reactions or modification processes. They are mostly composed of nitrates, sulphates, ammonium, organic compounds as well as trace metals when formed from combustion processes (Sioutas et al., 2005; Seinfeld & Pandis, 2006). Nucleation mode particles accounts for the greatest number of atmospheric particles and are found in high number concentrations near their sources. Their concentration in air is most commonly measured and expressed in terms of number concentrations of particles per unit volume of air (in contrast larger particles are measured in terms of mass concentration) (Kumar et al., 2011). Due to their small sizes and large surface area, they are highly chemically reactive. Collisions with each other and with particles in the accumulation mode are largely responsible for their relatively short atmospheric life time (few minutes up to hours). When inhaled these particles are deposited on the alveolar surface (Naga et al., 2005; West, 2008), thereafter, they can transport through the bloodstream or lymphatic system to vital organs (Oberdörster et al., 2004). In addition to their great efficiency to penetrate deep into the lungs, the large surface area may also account for their negative impacts on human health; the scientific evidence indicates that the larger the superficial area the greater the health impacts of particles (Tranfield & Walker, 2012).

The first research studies used the term ultrafine particles (Granqvist et al., 1976, 1977). Nowadays this term is still being predominantly used in aerosol and environmental sciences. However, in 1990’s the term nanoparticles became vastly popular as substitution of ultrafine particles and quickly became adopted in many fields, such as in medicine, material sciences and engineering. Both terms constitute a somewhat arbitrary classification of particles in terms of their size, indicating the significant role of this physical characteristic on particle fate in the air. Theoretically, nanoparticle is any particle with size range in nanometer scale (i.e. bellow 1000 nm; Anastasio & Martin, 2001; Kumar et al., 2010). British Standards Institution (BSI, 2005) defined nanoparticles as those that have one or more dimensions in the order of 100 nm or less. However in current scientific works, the size range definitions for nanoparticles differ significantly. The term nanoparticles was used for atmospheric particles in size ranges such as below 100 nm, 50 nm, 10 nm or occasionally even for particles smaller than 1 μm (Anastasio & Martin, 2001; British Standards Institution, 2005; Morawska et al., 2008). It is worth mentioning that Kumar et al. (2010) recently defined atmospheric nanoparticles as those bellow
300 nm (Fig. 2). Though this size range represents an overlap between particles from nuclei and accumulation mode, authors rationalized that the respective range includes more than 99% of the total number concentration of particles in the ambient atmospheric environments (Kumar et al., 2008a, 2008b, 2009, 2011), being potentially relevant for future regulations.

Therefore, when using the term nanoparticles it is necessary to define the size range of the particles in question. For the purposes of this chapter the term nanoparticles includes ambient nanosized particles < 100 nm (Oberdörster et al., 2005).

2.2. Sources and levels of nanoparticles

The major natural sources of atmospheric nanoparticles (Table 1) are atmospheric formations, vegetation and sea sprays. Volcanic eruptions or forest fires also produce, though sporadically, a large number of atmospheric nanoparticles (Kumar et al., 2011; Oberdörster et al., 2005).

The atmospheric formations of the particles include condensation of semi-volatile organic aerosols, photochemically induced nucleation, and/or nucleation through gas-to-particle conversion (Holmes, 2007). Concerning the latter, different nucleation mechanisms have been
assumed for the formation of atmospheric nanoparticles (Kumala et al., 2004): (i) binary nucleation of sulphuric acid and water; or (ii) ternary nucleation involving a third molecule, most likely is ammonia that is abundant in the troposphere and has been shown to enhance nucleation rates of sulphuric acid.

<table>
<thead>
<tr>
<th>Natural sources</th>
<th>Anthropogenic sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric formations</td>
<td>Engine combustions</td>
</tr>
<tr>
<td>Sea spray</td>
<td>Vehciles (petrol-, diesel-, alternative fuels)</td>
</tr>
<tr>
<td>Vegetation</td>
<td>Trains, ships, airplanes</td>
</tr>
<tr>
<td>Forest fires</td>
<td>Power plants</td>
</tr>
<tr>
<td>Volcanoes (hot lava)</td>
<td>Incinerators</td>
</tr>
<tr>
<td>Viruses</td>
<td>Various processes (smelting, heating, welding)</td>
</tr>
<tr>
<td></td>
<td>Industrial emissions</td>
</tr>
<tr>
<td></td>
<td>Commercial productions</td>
</tr>
</tbody>
</table>

**Table 1.** Sources of nanoparticles (Buseck & Adachi, 2008; Kumar et al., 2011; Oberdörster et al., 2005)

In remote sites, the formation of new particles is preceded by an increase in the atmospheric concentration of sulphuric acid (Holmes, 2007). Various studies reported an increase in particles number occurring about 1–2 h after an increase in sulphuric acid (Weber et al., 1996), being followed by a relatively small particle growth rate (between 1 and 2 nm h⁻¹; Birmili & Wiedensohler, 2000a; Weber et al., 1996, 1997). These findings point towards a linear relationship between the number of newly formed particles and the production rate of sulphuric acid. It is still not clear though whether at these environments the binary nucleation (i.e. water–sulphuric acid nucleation) is solely responsible for the formation of new particles or if a third specie, such as ammonia or an organic compound, is involved (i.e. ternary nucleation). In forests the mechanisms responsible for the formation and growth of atmospheric nanoparticles are not completely understood. Although sulphuric acid is one of the most likely candidates that might be responsible for the formation of the initial nanometre-sized particles (Riipinen et al., 2007), sulphur chemistry does not sustain enough sulphuric acid in the atmosphere to explain more than a small fraction of the observed particle size growth rate (Morawska et al., 2008). Several forest studies have concluded that particle formation can commonly occur from biogenic precursors (O’Dowd et al., 2002), some of them suggesting a direct relation between emissions of monoterpenes and gas-to-particle formation in regions substantially lacking in anthropogenic aerosol sources (Tunved et al., 2006). In addition the authors also estimated that forests provide an aerosol population of $1–2 \times 10^3$ cm⁻³ of climatically active particles (during the period of late spring to early autumn) thus representing a considerable source of global importance. In the marine environments the possible particle formation mechanisms are (Morawska et al., 2008): seawater bubble-burst process (Clarke et al., 2006; O’Dowd et al., 2004), ternary nucleation producing a reservoir of undetectable particles upon which vapours can condense (Kulmala et al., 2000, 2004), free tropospheric production with mixing down to the boundary layer (Raes, 1995), and generation of coastal iodine particles from macroalgal iodocarbon emissions (Kul-
mala et al., 2000; O’Dowd et al., 2004; O’Dowd & Hoffmann, 2005). Whereas the iodine-contain-
ing particles are not likely to play an important role globally, wind produced bubble-burst particles containing salt are ubiquitous in the marine environments. Clarke et al. (2006) have shown that sea salt aerosols produced by breaking waves are a significant constituent of particles with sizes as small as 10 nm, with 60% of the particles smaller than 100 nm in diameter. The authors estimated that in marine regions between 5% and 90% of the nuclei particles originate from the sea salt flux.

The implication of the above referred text is that nanoparticles are formed in the environments due to natural processes. Therefore, they are always present at some concentration levels even in the atmosphere of environments free from the immediate influence of anthropogenic activities. These concentrations should be considered as “natural background”. In addition, because the rates of formation and growth of nanoparticles differ significantly between various natural environments, there are significant variations in number concentrations of atmospheric particles. Whereas in marine environments particle number concentrations typically range between $10^2$ and $10^3$ particles cm$^{-3}$ (O’Dowd et al., 2004; Seinfeld & Pandis, 2006), the usual ranges in forests and rural continental regions are $10^3$ to $10^4$ (Birmili & Wiedensohler, 2000b; O’Dowd et al., 2002; Riipinen et al., 2007), though occurrence of forest fires may temporally increase these levels. Meteorological parameters, such as wind speed, precipitation, relative humidity and temperature also influence particle concentrations. Therefore, when evaluating particle concentrations in urban environments it is important to assess the respective background levels and to compare them with concentrations in urban environments in order to correctly estimate the magnitude of the anthropogenic impacts.

The number concentrations of nanoparticles in the atmosphere can vary by up to five or more orders of magnitude (from $10^2$ to $10^7$ particles cm$^{-3}$) depending on environmental conditions and source strengths (Kumar et al., 2010) but typically, in natural environments the particle number concentrations are approximately to 1-2 orders of magnitude smaller than those in urban areas (Kumar et al., 2010). Morawska et al. (2008) analysed concentration levels of 71 studies performed on nanoparticles in various environments, including those from clean background and rural background sites (Table 2). The authors found (Morawska et al., 2008), respectively, the mean concentrations of $2.6 \times 10^3$ and $4.8 \times 10^3$ particles cm$^{-3}$ for clean background and rural background sites compared to $42.1 \times 10^3$ and $48.2 \times 10^3$ particles cm$^{-3}$ for urban and street canyons; in urban areas anthropogenic sources, such as vehicular emissions are strong contributors of nanoparticles, thus much higher particle concentration levels were observed (Table 2). Road tunnels ($167.7 \times 10^3$ particles cm$^{-3}$) account for the highest concentrations. They can act as a trap for pollutants from vehicular emissions that is enhanced by the surrounding built-up environment that limits the dispersion of exhaust emissions (Van Dingenen et al., 2004).

There is no doubt that anthropogenic emissions constitute the major source of atmospheric nanoparticles in urban environments (Table 2). With respect to urban sites various studies have concluded that vehicle exhaust emissions represent a primary source of nanoparticle pollution in urban environments (Harrison et al., 1999; Shi & Harrison, 1999; Shi et al., 2001; Wählin et al., 2001) that might be responsible up to 86% of total particle number concentrations (Pey et
The vehicle emissions depend on many factors such as type of engines, fuels, lubricating oil, after-treatment or driving conditions. Typically particles emitted from diesel engines are in the size range 20–130 nm (Kittelson, 1998; Harris & Maricq, 2001). Diesel-fuelled vehicles make by far the greatest contributions to total number concentrations (Kumar et al., 2010) although in most of European countries their proportion is lower. In 2009 passenger diesel-fuelled cars in Europe accounted for to 9-10% (Sweden and Cyprus) to 62% (Luxemburg) but in 16 out of 21 European countries (where data is available) their proportion was less than 50% (EU, 2011). Large part of nanoparticles is also produce by heavy duty diesel vehicles (trucks, buses) that exhibit particle number emission factors one to two orders of magnitude larger than a typical petrol car (Ristovski et al., 2005, 2006). In comparison, particles from petrol-fuelled vehicles are in the size range 20–60 nm (Harris & Maricq, 2001; Ristovski et al., 2006), and their emissions vary significantly depending on the engine operating conditions; Graskow et al. (1998) reported that when driven at higher speed (~120 km h\(^{-1}\)) or during acceleration, the particle number emissions from petrol vehicles were similar to those observed from diesel vehicles.

<table>
<thead>
<tr>
<th>Site</th>
<th>Number of analyzed studies</th>
<th>Estimated concentration (\times 10^3) (particles cm(^{-3}))</th>
<th>Mean</th>
<th>Median</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean background</td>
<td>5</td>
<td>2.6</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>Rural background</td>
<td>8</td>
<td>4.8</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>Urban background</td>
<td>4</td>
<td>7.3</td>
<td>8.1</td>
<td></td>
</tr>
<tr>
<td>Urban</td>
<td>24</td>
<td>10.8</td>
<td>8.8</td>
<td></td>
</tr>
<tr>
<td>Street canyon</td>
<td>7</td>
<td>42.1</td>
<td>39.3</td>
<td></td>
</tr>
<tr>
<td>Roadside</td>
<td>18</td>
<td>48.2</td>
<td>34.6</td>
<td></td>
</tr>
<tr>
<td>On-road</td>
<td>2</td>
<td>71.5</td>
<td>47.0</td>
<td></td>
</tr>
<tr>
<td>Tunnel</td>
<td>3</td>
<td>167.7</td>
<td>99.1</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2.** Particle number concentrations in different environments (Morawska et al., 2008)

In general particles from vehicle exhaust may be divided into two main categories. Primary particles are directly emitted from the engines. These particles are mostly submicrometer agglomerates (30-500 nm) of solid phase carbonaceous material containing metallic ash (from lubricating oil additives and engine wear) and adsorbed or condensed hydrocarbons and sulphur compounds (Morawska et al., 2008). Secondary particles are formed in the atmosphere when hot exhaust gases are expelled from vehicle tailpipe; as they cool and condensate they form nuclei mode particles (typically smaller than 30 nm) that consists mainly of hydrocarbons and hydrated sulphuric acid (Morawska et al., 2008). On-roads studies (e.g. when a vehicle is being followed by a mobile laboratory; Kittelson et al., 2004, 2006; Casati et al., 2007) and those
performed near busy roads (Harrison et al., 1999; Ntziachristos et al., 2007; Rosenbohm et al., 2005; Westerdahl et al., 2005) reported large number of these particles.

The interactions between vehicle tyres and road can also generate particles of submicron sizes, although it was generally believed that tyre wear on the road contributes mainly to larger size (> 2.5 μm). Some more recent studies report (Gustafsson et al., 2008; Dahl et al., 2006) that considerable emissions of nanoparticles might be generated from road and tyre interactions, depending on surface, vehicle and driving conditions. As this source could be a significant contributor to particle number emissions, more research on this topic is needed.

The industrial sources of atmospheric nanoparticles include power plants, incinerators, or various industrial processes such as smelting or welding, heating operations (Oberdörster et al., 2005). Compared to vehicle exhaust emissions, their contribution to atmospheric nanoparticles is though much lower. In a study performed in Barcelona, Spain, Pey et al. (2009) investigated source apportionment of atmospheric particles in size range 13-800 nm (i.e. nuclei and accumulation mode) at an urban background site. The authors identified vehicular exhaust emissions (65%) and regional/urban background (24%) as the largest contributors to total particle number concentrations (mean of 17×10^3 particles cm^-3); industrial emissions accounted only for 2% of the total particle number. The levels of this contribution were similar in the study (Pey et al. (2009) to: photochemically induced nucleation (3%), sea spray (2%), and mineral dust (1%); unidentified sources accounted for 3%.

In the last decade nanoscience has been a dynamically developing field of scientific interest in the entire world (Aguar-Fernandez & Hullmann, 2007). Small size and relatively large reactive surface area of nanoparticles led to their increased use in a variety of fields such as in medicine, material sciences, electronics or energy storage (Helland et al., 2007). Thus engineered (i.e. manufactured) nanoparticles have become (apart from vehicle exhaust and industrial emissions) another important anthropogenic source of atmospheric nanoparticles. These nanoparticles are not intentionally released into the environment, though some release may occur during production, use and disposal phases of nanomaterial-integrated products (Bystrzejewska-Piotrowska et al., 2009). Their characteristics (sources, composition, homogeneity or heterogeneity, oxidant potential, exposure and emissions) differ from other atmospheric nanoparticles (Oberdörster et al., 2005). The engineered nanoparticles are nowadays incorporated into many products of daily use (pharmaceuticals, lubricants, cosmetics, pharmaceuticals, fillers, catalysts, electronic devices or other domestic appliances; Nel et al., 2006). The widespread use of manufactured nanoparticles in consumer products may dramatically increase potential environmental, occupational, and public exposures to these particles that may result in adverse health effects if they are not appropriately controlled. In addition, as nanotechnology has being nowadays used in various industries, it becomes responsible for the production of waste containing residue of nanomaterials; considering the unprecedented application of nanoparticles in various products, significant amounts of new-generation-waste will be certainly created in the near future (Bystrzejewska-Piotrowska et al., 2009).

In view of the comprehensive utilizations of nanotechnological applications, concerns regarding the potential health effects of engineered nanoparticles have been raised (Helland et al.,
2005). The available toxicological studies indicate (Nel et al., 2006; Oberdörster et al., 2005) that toxicity of engineered nanoparticles depends on specific physiochemical and environmental factors, implying that toxic potential of each type of nanoparticle has to be evaluated individually (Helland et al., 2007). Due to the great variability in used materials (e.g. titanium dioxide, silver, carbon, gold, cadmium and heavy metals; Kumar et al., 2010) it is thus not possible to generalize the toxicological impacts of the engineered nanoparticles. In addition size, shape, surface characteristics, inner structure and chemical composition may also play an important role in determining toxicity and reactivity (Maynard & Aitken, 2007; Nel et al., 2006).

2.3. Chemical composition of nanoparticles

The composition of atmospheric nanoparticles is highly variable. The source and formations influence their chemical composition and nanoparticles include components such as inorganic compounds (sulphates, nitrates, ammonium, chloride, trace metals), elemental and organic carbon, crystal materials, biological components (viruses), and volatile and semivolatile organic compounds (Oberdörster et al., 2005). They can carry toxic compounds such as heavy metals, dioxins, hydrocarbons and other organic chemicals (some of which are potentially carcinogenic) adhered to their surfaces which then increase their toxicity (Terzano et al., 2010). Apart the source-specificity, composition of nanoparticles also depends on geographical and meteorological parameters which in general lead to great differences in physicochemical properties among nanoparticles.

Several studies including a number of recent ones (Chen et al., 2010; Kim et al., 2011; Klems et al., 2011; Kudo et al., 2011) have evaluated the composition of atmospheric nanoparticles. However, at present, the knowledge on nanoparticles composition is far from comprehensive. The existent scientific studies are conducted at different ways, sample particles in a different size range, use different samplers, and focus on different aspects of particle chemical composition. Thus the reported data are not completely comparable across the studies. In their attempt to improve the current knowledge, Chow & Watson (2007) review and summarized the results of the existent studies. The authors analyzed 25 studies performed at various environments (rural, urban, industrial, coastal, roadside, traffic, city-centre, urban background, and etc.) and in various regions: two studies were conducted in Europe (Finland), four in Japan, three in Asia (one in China, two in Taiwan) and sixteen in USA; eleven US studies were performed in California, eight of them were from different locations within the Los Angeles metropolitan area. Concerning the chemical composition the authors concluded that organic material including polycyclic aromatic hydrocarbons was the most abundant portion of atmospheric nanoparticles in most, but not all environments. High elemental concentrations were found in nanoparticles from industrial sites with potassium, calcium and iron as important elements. Potassium originates from biomass burning, and calcium is used as an oil additive; condensed iron vapors are often found in industrial processes. Much of the nanoparticles appeared to be semi-volatile, consistent with being comprised of organic materials such as hopanes from engine oils or condensed secondary organic aerosol such as organic acids. However, authors emphasize the necessity to conduct more studies on particle chemical
composition in order to provide a more complete understanding on the chemistry of atmospheric nanoparticles and local variations.

3. Regulatory aspects

During last two decades the exponentially growing interdisciplinary research on air quality and health has clearly demonstrated increased incidence and the prevalence of respiratory diseases along with increased air pollution. Particles have emerged as the most dangerous pollutants due their adverse health effects going far beyond the simple toxicity to the lung. The results of the conducted epidemiology studies were so relevant that USEPA and EU have implemented strategies to protect public health which resulted in establishment of regulatory limits of atmospheric particles (PM$_{10}$). As the ongoing research emphasized the importance of smaller (i.e. fine) particles the new PM$_{2.5}$ standards were proposed and implemented in most of developed countries (Table 3). However, the reduction of atmospheric particulate emissions is nowadays required especially in rapidly developing countries, such as Brazil, China or India but they are only slowly moving towards implementation of these standards (Slezakova et al., 2012); there are still a number of countries, such as Pakistan where any regulatory limits for atmospheric particles have not been proposed yet.

<table>
<thead>
<tr>
<th>Country</th>
<th>Pollutant</th>
<th>Targeted limit</th>
<th>Note</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>European Union</td>
<td>PM$_{10}$</td>
<td>24h mean: 40 μg/m$^3$</td>
<td>Not to be exceeded more than 35 times per calendar year</td>
<td>Directive 2008/50/EC</td>
</tr>
<tr>
<td></td>
<td>PM$_{2.5}$</td>
<td>Annual mean: 50 μg/m$^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>USA</td>
<td>PM$_{10}$</td>
<td>24h mean: 150 μg/m$^3$</td>
<td></td>
<td>USEPA, 2006</td>
</tr>
<tr>
<td></td>
<td>PM$_{2.5}$</td>
<td>24h mean: 35 μg/m$^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Annual mean: 15 μg/m$^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Canada</td>
<td>PM$_{2.5}$</td>
<td>24h mean: 30 μg/m$^3$</td>
<td></td>
<td>Canadian Council of Ministries of Environment, 2003</td>
</tr>
<tr>
<td>Australia</td>
<td>PM$_{10}$</td>
<td>24h mean: 50 μg/m$^3$</td>
<td></td>
<td>Australian Government, 2012</td>
</tr>
<tr>
<td></td>
<td>PM$_{2.5}$</td>
<td>24h mean: 25 μg/m$^3$</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>Annual mean: 8 μg/m$^3$</td>
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<td></td>
</tr>
<tr>
<td>Japan</td>
<td>PM$_{10}$</td>
<td>24h mean: 100 μg/m$^3$</td>
<td></td>
<td>Government of Japan, 2012</td>
</tr>
<tr>
<td></td>
<td>PM$_{2.5}$</td>
<td>24h mean: 35 μg/m$^3$</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>Annual mean: 15 μg/m$^3$</td>
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</table>

Table 3. Air quality standards for atmospheric particles in selected countries
Unlike fine or coarse particles, the regulatory aspect of nanoparticles has not been addressed yet. The difficulty lies as to which metric of nanoparticles would be the most adequate. Several generic and specific characteristics of particles such as chemical composition, size, geometry or surface area have been discussed (Kumar et al., 2010, 2011) but no conclusion has been reached yet. The mass-based paradigm of PM$_{10}$ and PM$_{2.5}$ regulator limits is not applicable to nanoparticles as their distribution is not dominated by mass but particle number. Some studies have suggested that the particle number concentrations of ultrafine particles (i.e. smaller than 100 nm) are an important parameter as size range comprises the major proportion (about 80%) of the total number concentration of ambient nanoparticles, but negligible mass concentration. Reliable characterization of nanoparticles in the air is thus vital for developing a regulatory framework. At national levels air quality agencies should be encouraged to integrate nanoparticle measurements in their monitoring networks (number and size distributions measurements). Such initiatives might provide comprehensive data and information necessary to correctly address regulatory aspects of atmospheric nanoparticles in order to prevent the public exposures.

4. Health impacts

Due to intensive research, there is an emerging evidence that exposure to nanoparticles may adversely affect human health (Stölzel et al., 2007). The nanoparticles enter human body through the skin, lung and gastrointestinal tract (Nel et al., 2006). When they are inhaled, their behavior differs from coarse particles. Their small size allows them to be breathed deeply into the lungs where they are able to penetrate alveolar epithelium and enter the pulmonary interstitium and vascular space to be absorbed directly into the blood stream (Terzano et al., 2010). They may also translocate within the body to the central nerve system, the brain, into the systemic circulation and to organs like the liver (Helland et al., 2007; Figure 3). They are more reactive and toxic due to the larger surface areas, leading to detrimental health effects such as oxidation stress, pulmonary inflammation and cardiovascular events (Buseck & Adachi, 2008; Nel et al., 2006).

Though the toxicological studies have provided evidence of the toxicity of nanoparticles, epidemiological evidence of the health effects is limited. Currently, there is also no quantitative summary of concentration-response functions for these particles that could be used in health impact assessment (Hoek et al., 2010). Unlike for coarse and fine particles there are relatively few epidemiological studies on the health effects of atmospheric nanoparticles. The first conducted studies on atmospheric nanoparticles have been panel studies, which generally showed associations between short-term exposure to nanosized particles and occurrence of acute respiratory symptoms and lung function (Ibald-Mulli et al., 2002; Peters et al., 1997; Penttinen et al., 2001a, 2001b). Some of these studies have suggested that nanoparticles might be even more strongly associated with adverse respiratory outcomes than fine particles (Peters et al., 1997; Penttinen et al., 2001a) whereas other studies found similar associations in health outcomes of nano and fine particles (von Klot et al., 2002; Pekkannen et al., 1997, Penttinen et al., 2001b).
Up to this date, only few epidemiological studies have assessed more severe end points such as daily, and cause specific mortality and hospital admissions (Stölzel, et al., 2007; Wichman et al., 2000); there are no epidemiological studies on long-term exposure to atmospheric nanoparticles.

Although lungs are the primary target of nanoparticles, cardiovascular detrimental consequences due exposure to nanoparticles have also been observed in some epidemiological studies (Kettunen, et al., 2007; Rückerl et al., 2007). Specifically, the “Exposure and Risk Assessment for Fine and Ultrafine Particles in Ambient Air” (i.e. ULTRA) study investigated the health effects of nanoparticles in three European cities (Amsterdam, Erfurt, Helsinki), where daily number concentrations levels of nanoparticles in air were similar (Ruuskanen et al., 2001). The authors followed a cohort of 131 patients aged 40-84 with established coronary heart disease with biweekly submaximal exercise tests over a 6-months period. It was observed that the risk of developing ischemia during exercise was significantly elevated at 2 days after exposure to increased environmental levels of nanoparticles (Pekkanen et al., 2002). The importance of this observation is that it highlights myocardial ischemia as a significant potential mechanism responsible for the adverse cardiac outcomes associated with poor air quality (Terzano et al., 2010). In addition particulate pollution including nanoparticles was associated
with decrease in blood pressure (Ibald-Mulli et al., 2004). The study thus started to provide an understanding of how nanoparticles may affect cardiovascular health.

5. Environmental impacts

5.1. Visibility impairment

Impairment of the visibility involves degrading of the ability to perceive the environment. Atmospheric suspended particles are the most important factor in the visibility reduction (Boubel et al., 1994). The reduction of visibility is caused by build-up of the atmospheric particles that absorb or scatter light from the sun (Horvath, 2008); though light scattering by particles is the most important phenomenon responsible for impairment of visibility. The size of particles plays a crucial role for the interaction with light, but so far the existing links between visibility impairment and mass concentrations have been established for larger particles (Boubel et al., 1994; Strawa et al., 2010). Shape and composition of particles are also relevant for visibility reduction; carbon particles may contribute 5–40% of overall visibility reduction through light absorption in polluted areas, whereas particles containing sulphate, organic carbon and nitrate species may cause 60-95% of visibility reduction (Kumar et al., 2010). Finally, visibility impairment is affected by meteorological parameters; it increases with relative humidity and atmospheric pressure and decreases with temperature and wind speed (Kim et al., 2002; Tsai, 2005). In general the role of nanoparticles in visibility impairment is still unclear. However, diesel vehicles emit large number of sulphate and carbonaceous nanoparticles. Particles of these compositions reduce visibility which suggests that nanoparticles might be relevant for visibility impairment. Therefore, deeper understanding of nanoparticles role in visibility impairment is necessary.

5.2. Climate change

Climate system, atmospheric chemistry and even life on the Earth are dependent on solar radiation (Boubel et al., 1994). Approximately 30% of the incoming solar energy is reflected back to space. The remaining 70% is absorbed by the surface-atmosphere system of the Earth. This energy heats the planet and the atmosphere. As the surface and the atmosphere become warm, they release the energy in form of infrared radiation. This process continues until the incoming solar energy and the outgoing heat radiation are in balance. This radiation energy balance provides a powerful constraint for the global average temperature of the planet (Ramanathan & Feng, 2009). Atmospheric greenhouse gases (such as like carbon dioxide and methane) and particles affect the climate by altering the incoming solar and outgoing thermal radiations. In other words changing the atmospheric abundance or properties of these gases and particles can lead to a warming or cooling of the climate system. The influence of a factor (pollutant) that cause change of climate system are typically evaluated in terms of its radiative forcing, which is an estimate of how the energy balance of the Earth-atmosphere system is influenced when the factor in question is altered (IPCC, 2007).
Atmospheric nanosized particles are the main precursors of larger particles. They promote their growth and modify the optical properties thus affecting the radiative properties of the atmosphere. It was generally believed that particles reflect sunlight back to space before it reaches the surface, and thus contribute to a cooling of the surface (i.e. negative radiative forcing; Monks et al., 2009). During time as the concentrations of particles increased (along with greenhouse gases) their cooling effect has masked some of the greenhouse warming (Ramanathan & Feng, 2009). This masking effect could be relative large considering that estimated negative radiative forcing of particles is $-1.2 \text{ W m}^{-2}$ compared with $+2.63 \text{ W m}^{-2}$ for greenhouse gases ($+1.66 \text{ W m}^{-2}$ for carbon dioxide, $+0.48 \text{ W m}^{-2}$ for methane and $+0.16 \text{ W m}^{-2}$ for nitrous oxide, $+0.34 \text{ W m}^{-2}$ for halocarbons; IPCC, 2007). However, in the last years the view of particle role in climate change has deepened. It was found that atmospheric particles may also enhance scattering and absorption of solar radiation thus causing direct warm-up (i.e. positive radiation; IPPC, 2007). Especially, carbonaceous particles are considered as one of the major contributors to global warming (i.e. $+0.34 \text{ W m}^{-2}$); if they are coated with sulphate or organic compounds their radiative forcing can increase up to about $+0.6 \text{ W m}^{-2}$ (Kumar et al., 2010).

Indirectly nanoparticles can also cause a negative radiative forcing through changes in cloud formations and properties (IPCC, 2007). They can act as cloud condensation nuclei and modify size and number concentrations of cloud droplets. In clean air, clouds are composed of a relatively small number of large droplets. As a consequence, the clouds are somewhat dark and translucent. In polluted air with high concentrations of particles (such as urban areas) water can easily condense on the particles, creating a large number of small droplets. These clouds are dense, very reflective, and bright white. Due to the decrease of the size of water droplets these clouds are less efficient at releasing precipitation. They cause large reductions in the amount of solar radiation reaching Earth’s surface, a corresponding increase in atmospheric solar heating, changes in atmospheric thermal structure, surface cooling, disruption of regional circulation systems such as the monsoons, suppression of rainfall, and less efficient removal of pollutants (Ramanathan & Feng, 2009). In general the indirect effects of particles are only partially understood. The interactions between aerosol particles (natural and anthropogenic in origin) and clouds are complex and most instruments cannot measure aerosols within the clouds. Climatologists thus consider the role of clouds to be the largest single uncertainty in climate prediction.

The close relation between climate and air quality also reflects on the impacts of climate change on air pollution levels. For example particle pollution levels are strongly influenced by shifts in the weather (e.g., heat waves or droughts; EEA, 2012a). While closely related, climate change and air pollution have mostly been treated as separate problems. At the international level, various efforts have helped to reduce air pollution levels. The largest reductions have been achieved for emissions of sulphur dioxide which decreased in Europe by 82% between 1990 and 2010 (EEA, 2012b). The implementation of EU regulation limits setting levels of sulphur dioxide in urban areas and various political actions to control urban atmospheric emissions (i.e. sulfur abatement technologies in industrial facilities, EEA, 2011; introduction of fuels with reduced levels of sulfur, Directive 98/70/EC; EN 590/2004) have contributed to these reduc-
tions. In addition, significant reductions were also obtained for emissions of air pollutants that are primarily responsible for formation of harmful ground-level ozone: non-methane volatile organic compounds (56% reduction) and nitrogen oxides (47% reduction; EEA, 2012b). However, based on the future climate scenarios (and in the absence of additional emissions reductions) the IPCC still projected declining air quality in cities into the future as a result of climate change (USEPA, 2012b). In agreement, USEPA has concluded that climate change could have various negative impacts on national air quality levels that included both increases and decreases in particle pollution (USEPA, 2009). Thus in order to protect human health and environment, joined efforts to control air pollution and mitigate climate change have to be done in future: air pollution abatement measures may help protect the regional and global climate whilst taking certain climate change measures may yield additional benefits through improved local and regional air quality.

6. Conclusion

Atmospheric nanoparticles represent an area of growing health concern. Although our understanding of the ambient nanoparticles and their behavior has increased considerably in recent years, the magnitude of the impacts of nanoparticles on human health and the environment has still not been fully understood. Lack of answers from epidemiological studies in relation to atmospheric nanoparticles and the absence of the exposure-response relationships also mean that currently it is not possible to develop health guidelines, a basis for national regulations. Thus, a multidisciplinary approach including atmospheric scientists, nanomaterial engineers, epidemiologists, clinicians and toxicologists is necessary to further investigate sources, generation, physicochemical characteristics and potential harmful effects of nanoparticles. This knowledge would allow better understanding of the potential impacts of the particles on the environment and health and would provide scientific foundation for development of strategies to protect public health.

The knowledge on the characteristics of engineered nanoparticles is in general very limited. Though these nanoparticles appear in smaller concentrations than other atmospheric nanoparticles they may pose much larger health risks (Oberdörster et al., 2005). Therefore, the future studies need to consider the specificity of these nanoparticles and the new kinds of environmental and health impacts resulting from the release of these nanoparticles.

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