Review

# The pollutant particle size and chemistry matters

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Abstract: The air is not the same as thousands and hundreds of years ago. In the air, suspended particles originate from natural phenomena like dust storms or volcanic activities, as well as anthropogenic pollutants such as fuel engine exhaust and everyday activities at home. The total particles in the air can be classified by sizes, such as PM10, PM2.5 or ultrafine particles. However, there are many other important factors in addition to the particle size, influencing the particle behavior and affecting our health. The surface area, chemical and biological composition, aspect ratio, and the charge are all factors characteristic of particles. OoC microfluidic chips are very useful for the pollutant toxicity measurements on various body tissues. A better understanding of pollutants will help to trace these to the potential sources. The data from the on-the-ground and satellite monitoring can be integrated into models, helping to predict and prevent pollution exposure.

Keywords: Aerosols, Particulate Matter (PM), PM2.5, nanoparticles, toxicity, source, Organ-on-a-Chip (OoC)

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### 1. Introduction

When the living conditions, including the air we breathe, are of good quality, we even do not think about it. The air for the on-the-land living organisms is a medium that we interact all the time. It is like the water for the fishes and other aqua organisms. Mainly lungs and our skin are exposed to the air. The direct contact allows any particles present in the air gasses, to enter the lungs or even the skin. That happens especially if the defense immune system is compromised.

Everyone would like to live in as healthy as possible environment. However, the Earth atmosphere is associated with the natural particle producing phenomena like volcanic activities or forest fires. Humans are additionally exposed to the anthropogenic particle source, such as home-cooking. The recent petroleum oil discovery and industrial revolution brought a range of new and some untested particle pollutants originating from combustion vehicles, plastics or even microand nanosized bead plastic additives [1]. This is a contemporary situation as the pollutants change over time. The pollution sources should be minimized, contained and if possible, completely stopped.

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#### 2. Aerosols

The air pollution has adverse effects on people daily lives and the health. Especially the chemical substances and small particles in the air are dangerous through chronic exposure to the body. All the small and microscopic solids or liquids, which are suspended in the air, constitutes the air aerosols. The origins of the aerosols are usually from the land or the sea, when the wind pickups the soil or the salty water particles and suspends into the air, further carrying over the hundreds or thousands of kilometers. The examples of the aerosol origin can be the salt spray containing lots of components present in the seawater (such as sodium chloride (NaCl), magnesium (Mg²+), calcium (Ca²+), potassium (K-) or sulfate (SO₄²-) ions), or dust storms, formed by winds picking up the sand and soil particles, mainly mineral particles from the Earth's crust. While the forming salt sprays are most common over the oceans, the dust storms are a naturally occurring form of pollution in some of the Middle East, African and Asian countries.

The aerosols are formed either both by natural and the anthropogenic (it is also called a human-made) pollution. The main source of the anthropogenic pollution originates from the burning of the fossil fuels, which includes the entire fossil fuel industry. The incomplete combustion, either by coal plants, biomass (wood or other waste), or the exhaust from motor engines produce all kinds of pollutants. We cannot expect the final combustion products to be just water (H<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>). The petroleum and oil itself contain various byproducts and Sulphur-containing complex molecules. By burning these, Sulphur oxides (SO<sub>x</sub>, i.e., SO<sub>2</sub>,) are released. Sulfur oxide may be further oxidized in the air (for example in the presence of catalyst nitrogen dioxide NO<sub>2</sub>), forming the dangerous sulphuric acid (H<sub>2</sub>SO<sub>4</sub>).

Incomplete combustion of organic matter promotes the release of carbon monoxide (CO). It is clear that acute CO poisoning is most dangerous, as CO enters the lung, and binds preferentially to hemoglobin, myoglobin and mitochondrial cytochrome oxidase, thus restricting the oxygen supply [2,3]. The CO gas can also cause the brain lipid peroxidation (degradation of unsaturated fatty acids), leading to the necrosis of the white matter [4,5]. The chronic poisoning of CO is also very dangerous. Even long-term exposure to the low levels of CO may cause the persistent cerebral (brain) related issues (such as memory loss, depression, headaches) [6], and may worsen cardiovascular symptoms [7]. Usually, removal of the CO source, the symptoms resolve, unless there is an acute CO poisoning.

The haze, smoke dust, particulate air pollutants, fume, mist, and fog all constitute the aerosols, mainly with the diameter size of <1  $\mu$ m. The suspended particles in the air stay afloat depending on the particle size and other conditions such as temperature and humidity. Usually, the smaller the particles, the longer they stay afloat. The particles of size <10  $\mu$ m may stay in the air for several weeks [8]. Nano-sized particles are also produced indoors, during some industrial processes (i.e., TiO<sub>2</sub> nanoparticle production) or mechanical processes (drilling, abrading, sanding, shredding, etc.). The industrial workers should be conscious of the danger and protect themselves from the released nanosized particles.

We should not underestimate the aerosols in the air, as these may seem harmless, because they may absorb other pollutants. One of these natural sources is volcanic eruptions [9,10], which releases lots of hydrogen sulfide (H<sub>2</sub>S) and acids such as hydrochloric acid (HCl) and sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) into the air. The volcanic gasses represent aerosols contributing to further chemical reactions in the atmosphere which return to the Earth as acid rains.

#### 3. The size of the Particulate Matter (PM)

All the microscopic solid or liquid matter suspended in the atmosphere can be called as Particulate Matter (PM). The size of PM matters (Figure 1). The gaseous contaminants are of a size smaller than viruses (0.1 – 10 nm). The soot, to bacco smoke, and smog are of the size of small viruses or the suspended atmospheric dust (0.01 – 1  $\mu$ m). The oil smoke, fly ash and cement dust are of the size of some allergens (such as dust mites), the bacteria, the mold spores and pollen (1 – 100  $\mu$ m).

#### 3.1 The total particles in the air

The pollutants in the air can also be grouped based on the particle size influence on human health (Table 1). A high-volume air sampler (sampling more than 1500 m³ of air over a 24-hour period) is capable of measuring the total suspended particulate matter (TSP) which represents the total number of particles suspended in the atmosphere. The biggest particles can be denoted as Suspended Particulate Matter (SPM). The definition and particle size depends largely on the instrumentation used for the collection and estimation of the particle size. For example, dust monitoring equipment from the DustWatch company measures SPM by a cut off at 100  $\mu$ m. Then the maximum particle size collected is as close to 100  $\mu$ m as possible [11]. A subclass of SPM smaller particles is defined as Respirable Suspended Particulate Matter (RSPM) or simply Respirable Suspended Particulates (RSP). RSPM is considered more dangerous to health, and the ratio of RSPM to SPM is more important value than SPM alone and may be specific to an area. RSPM is also named as P10 or PM10, although RSPM includes PM10, PM2.5, and other fine particles.

#### 3.2. PM10

PM10 are mainly produced by industrial sources, combustion processes, and vehicles.

It is easy to define PM10 as the particles less than or equal to 10  $\mu$ m in diameter. However, this definition is not precise, as the equipment measures the median diameter of the particles. In this way, the PM10 represents the concentration of the median particle size of 10  $\mu$ m. Understandably, 50% of the particles will have a diameter less than 10  $\mu$ m, and 50% of the particles will have diameters larger than 10  $\mu$ m.

There are many ways to measure the PM10 number. For example, filter-based gravimetric samplers have the sampling inlet that is directly connected to a filter substrate. Following completion of the sampling period, the PM10 mass collected on the filter is weighted. This procedure, especially the filter changing can be automated. Another method for measuring PM10 in the air is using the so-called Tapered element oscillating microbalance analyzer (TEOM). TEOM is capable of continuously measuring the concentrations of air particles (for example, providing the measurement result every one hour). TEOM has a replaceable Teflon-coated glass filter cartridge (which does not need to be changed as often as in high-volume air gravimetric samplers), and the estimated precision is +/-  $0.5 \mu g/m^3$ . The working principle of TEOM is a microbalance, measuring the accumulated weight of the cut-off particles (for example PM10) on a filter cartridge. The accumulated particle weight on the filter is calculated based on the linear dependence of the change of the natural frequency of oscillation and the weight. With the flow rate known, it is possible to calculate also the particle concentration in a given sample.

Besides the filter-based gravimetric samplers (TEOM) there are other methods used in practice for PM measurements such as  $\beta$ -attenuation analyzers, optical analyzers, the black smoke method and personal samplers [12]. Currently, the gravimetric samplers and TEOM are the most popular methods in the practical applications.

#### 3.3. PM2.5

While PM10 particles are generated by both combustion and non-combustion processes (such as industrial processes, motor vehicle engines, the sea salt, windblown dust, and fires), the PM2.5 particles are generated mainly by combustion processes (such as fires, industrial boilers, solid fuel heaters, and motor vehicle engines). The research indicated that the smaller particles, especially the PM less than 2.5  $\mu$ m in diameter are more closely associated with adverse health effects than using measurements of PM10 particles [13]. PM2.5 particles, as well as PM10, are invisible to the naked eye. Simply compare the particle of the size of 2.5 or 10  $\mu$ m with the hair about 60  $\mu$ m in diameter. Understandably, some definitions of PM2.5 as particles only smaller than 2.5  $\mu$ m are oversimplified. According to the International Standards Organization (ISO) [14], the PM2.5 value represents the "particles which pass through a size-selective inlet with a 50 % efficiency cut-off at 2.5  $\mu$ m

aerodynamic diameter" [15]. The PM2.5 fraction is a standard size fraction where the particle median diameter is 2.5  $\mu$ m. Understandably, the PM2.5 contains both the bigger and smaller particles of the size of 2.5  $\mu$ m.

The PM2.5 fraction of PM differs from the PM10 just in the size of the particles included, and some same instrumentation can be used to measure PM2.5, by applying different filters. In practice, the measurement of PM2.5 is more complicated, as the total mass of PM2.5 particles is lower compared to the bigger particles. Therefore, the coarse fraction should be excluded, and more accurate methods are required. The methods for the smaller size PM2.5 fraction follow the same principles as those for PM10 measurement. The reference methods for PM2.5 are not capable of producing real-time data. Therefore, equivalent methods are used. Commercial companies sell instruments suitable for PM2.5 measurements. A group of non-reference manual gravimetric samplers is called Partisols (i.e., such as Partisol 2025 instrument) [16,17]. The gravimetric samplers employ a sequential sampling system of filters that enables up to several fixed 24-hour period particulate samples, requiring visits every two weeks to exchange filter cassette magazines.

The automatic instruments Filter Dynamic Measurement System (FDMS) (made by Thermo) [18] and Beta Attenuation Monitor (BAM) (made by Met-One) [19,20] deliver automatic data. The FDMS is based on TEOM. On FDMS, both volatile and non-volatile measurements are made.

In practice, measurement of the mass is complicated by the presence of some other (semi-volatile) particles, humidity, and other factors. Therefore, the PM2.5 metric does not correspond to definite physical components of the air but is in effect defined by the measurement method.

### 3.4. Ultrafine Particles

The most health-damaging particles are in nanometer size that are capable of passing through the cell membrane, migrating to other organs such as the brain, reaching and damaging the cardiovascular system [21]. The ultrafine particles (UFP) are commonly defined as particles in the size of <100 nm (<0.1  $\mu$ m) in diameter. UFP is also labeled as PM0.1.

Understandably, the measurements are based not on the mass (as UFP contribute very little to the mass), but on trying to quantify the particle number in the air. Instead of conventional light scattering methods (which cannot detect the ultrafine particles), the Condensation Particle Counter (CPC) is used [22,23]. The sampled air passes through a compartment that is saturated with alcohol vapor, which will condense on the small particles. The particles will grow in size and are counted in an optical detector. The CPC is capable of measuring the particles within the range of 3 – 2000 nm. Another method for ultrafine particle detection and counting is the Scanning Mobility Particle Sizer (SMPS) [24,25], where particles are separated according to the electrical mobility. The particle concentration can be measured for the particles within the range 11 – 450 nm.

As we mentioned previously, the smaller and lighter particles (such as in size of <10  $\mu$ m) tend to stay in the air longer, and the particles in the size of <1 nm, stay even for weeks. For example, the small particles such as Diesel particulate matter (DPM) are in size of <100 nm, are emitted from diesel engines, and have the highest concentration near the source of emission (such as highways or cities). The small particles are usually removed by precipitation (such as rain).

#### 4. The factors influencing the particle effects

While it is a well-established the fact that the particle size has an enormous impact on cell and tissue (and therefore, our body) health, other factors are as important. The particle surface area is related to the particle size. Nanoparticles follow collective behavior that could be described by quantum physics. Particle chemistry (identifying what the particle is made of) is also important for its reactivity and interaction with other chemicals and the cells. Biologicals such as DNA and proteins on the particles have an impact on our cells, especially affecting the immune system.

#### 4.1. Particle surface area

Multiple studies support the view that the health hazard is related to the particle size, that is the smaller particles, the deeper they are capable of penetrating into our lungs, and the cardiovascular system, then accumulates and damage our organs. The measurement methods, however, usually measure the total mass of particular fraction (PM10, PM2.5). From this measurement, the particle count (a numerical quantity) can be derived. Some legislative limits for the diesel engine emissions are based on mass. However, the total mass of specific fraction of the particles is not a proper measure of the health hazard. For example, one  $10~\mu m$  diameter particle has the same mass as 1 million particles of 100~nm diameter. Understandably, one larger particle is less hazardous than million smaller particles which are more capable of entering the alveoli.

We provide a simple explanation in mathematical terms, how the cube can be divided into eight smaller cubes, with following the increase of surface area (Figure 2). The volume, however, remains constant. We suppose a cube  $B = \{(x,y,z)|0 \le x \le l, 0 \le y \le l, 0 \le z \le l\} = [0,l] \times [0,l] \times [0,l] \times [0,l]$  is given. Then the surface area of the cube is  $s = 6l^2$ . If the cube is divided into sub-boxes, then the surface area increases. We do this by dividing each of the intervals [0,l] into n sub intervals  $[l_{i-1},l_i]$  of equal width  $\Delta l = \frac{l}{n}$ . The planes through the endpoints of these sub-intervals parallel to the coordinate planes divide the box B into  $n^3$  sub-boxes  $B_{ijk} = [l_{i-1},l_i] \times [l_{j-1},l_j] \times [l_{k-1},l_k]$ . Each sub-box has surface area  $\Delta s = 6\Delta l^2 = 6\frac{l^2}{n^2}$ . Then we form the sum  $T_s = \sum_{i=1}^n \sum_{j=1}^n \sum_{k=1}^n \Delta s = n^3 \Delta s = n6l^2 = ns$ , to obtain the total surface area, where s is the surface area of the cube s. So, the total surface area after dividing the box into s sub-boxes is n times as much as the surface area of the box s, that is s = s = s. For example, in Figure 2, s = s and the box is divide into s = s sub-boxes. The surface area of the box is s = s

An important factor for the health is the particle surface area. Comparing the same mass fractions of different size particles, the smaller particles will have proportionally bigger the surface area, as there are much more particles in smaller diameter size fraction, compared to the bigger diameter particles (Figure 2). The particle interacts with the human cells and cell compartments through its surface, inhibiting the vital enzymatic reactions [26]. There are no straightforward methods to measure the particles surface area. One of the methods utilizes an attachment of heavy labeled atoms (such as  $^{211}$ Pb) to the particles. The aerosol particles are captured on a filter, and the signal is measured by an  $\alpha$ -counter (such as epiphaniometer). The measured signal corresponds to the transferred mass, which is proportional to the particle surface area [27]. Another method to measure the particle surface area is based on measuring the particle number size distributions. With the estimated particle geometry, the distributions can be converted to surface area. Usually, an SMPS is used for measuring smaller particles (with diameters from 2.5 nm to 1000 nm) [24], and the Aerodynamic Particle Sizer (APS) is used for the larger particle size fractions (0.5 to 20 µm) [28,29].

The surface area plays a huge role when the biological molecules or chemicals interact with the surface (Figure 2). As an example, the large surface may adsorb some proteins (such as polymerases) or other molecules, which become inactivated and not available anymore for the reactions [26]. In this publication, we demonstrated the potential inhibition of the biological molecule (such as an enzyme) on the microfluidic material surface. For the small pollutant particles, it is opposite. The large pollutant surface may act inhibitory on the lung cells.

The data for particle number, size, surface area, and morphology are very important. It is confirmed and well acknowledged that the respirable (PM10) and fine suspended particles

(PM2.5) are more dangerous to health than larger particulate up to 100 μm. There is clear evidence that both PM2.5 and PM10 cause additional hospital admissions and premature deaths of the old and sick on high pollution days. PM has a significant contributory role in human all-cause mortality and in particular in cardiopulmonary mortality. Even the short-term particle exposure (such as during dust storms or other pollution episodes) worsens the asthma symptoms and even worsening

the general condition leading to lower level of activity. A recent review by Schulze *et al.* describes the impact of various pollutant particles on human health [30].

Even modern diesel engines emit lots of particles (such as DPM) in size range of 100 nm (0.1  $\mu$ m). These soot particles can carry carcinogens like benzopyrenes which are adsorbed on the particle surface. Currently, the car manufacturers are trying to minimize the problem with various particulate filters. That does not work well in a weak regulatory environment, such as in developing countries where the filters in the cars are not present.

#### 4.2. Chemical particles composition

Knowing the particles chemical composition helps to identify the source and allows estimating the particle distribution. There have been attempts to determine the particle composition. In an experiment in 2008, PM2.5 particles were collected. The further analysis of the composition indicated the three components that account for a large proportion of the total mass: organic carbon (organics), nitrate ( $NO_3$ °), and sulfate ( $SO_4$ <sup>2</sup>) [31].

Primary (from road traffic), as well as domestic (oil and solid fuel) combustion contributes to the elemental carbon (C), as well as the organics. Studies showed a clear link between the traffic emissions and its significant contribution to black carbon concentrations. We denote the black carbon as the sooty black material emitted from car engines and other sources that burn fossil fuel. Hourly measurement over the day indicated that the black carbon concentrations are most significant during the evenings, which is produced by the use of solid or liquid fuel for domestic heating [32].

The emissions from the road traffic, such as road abrasion or tire and brake wear are non-exhaust emissions of PM2.5. Understandably, emissions increase with increasing traffic levels. Non-exhaust traffic emissions also produce iron-rich (Fe) dust. It is important to measure iron in the particles, as it allows to understand the pollution source since iron is a marker for non-exhaust vehicle emissions. While the electric-powered cars considered as "clean cars", they mainly would contribute to the road and tire abrasion, as well as the brake wear pollution sources. The construction industry (including construction and demolition, mineral and cement handling), as well as wind-blown soil, produce particles rich in calcium (Ca²+) salts. Sodium chloride (NaCl) in the dust usually comes from the sea salt.

An increase in nitrate (NO<sub>3</sub>-) was observed in some instances of high PM2.5 pollution [33,34]. The authors state that it is important to understand the origins of higher nitrate concentrations in PM2.5 particles and suggest measuring the air quality and the particle chemistry both on the roads and in the rural areas. It is recommended to have the following smallest set of accessed chemical species in the measurements: elemental carbon (EC), organic carbon (OC), sodium (Na+), potassium (K<sup>+</sup>), calcium (Ca<sup>2+</sup>), magnesium (Mg<sup>2+</sup>), chloride (Cl<sup>-</sup>), ammonium (NH<sup>4+</sup>), nitrate (NO<sup>3-</sup>), sulfate (SO<sub>4</sub><sup>2</sup>-), and iron (Fe). Interestingly, the chemical correspondence of nitrate and sulfate with ammonium indicated the neutrality of the particles and the complete chemical formula is ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) and ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>). One can imagine the complex interaction of ammonium (NH3) (which is usually in excess) with NOx and SO2, whereas the ammonium level is controlled by strong acids such as hydrochloric (HCl), nitric (HNO3) and sulphuric (H<sub>2</sub>SO<sub>4</sub>) acids. A secondary pollutant PM sulfate is stable in the atmosphere and, once formed irreversibly, will not decompose back to ammonia and sulphuric acid vapors under normal atmospheric conditions. However, the secondary PM ammonium nitrate (NH4NO3) is thermally unstable and may revert to nitric acid (HNO3) and gaseous ammonia (NH3) within minutes to hours depending on atmospheric conditions.

Primary emissions from road traffic also contribute to regional secondary PM through the oxidation of emissions of nitrogen oxides. The primary pollution sources do not contribute to all of the PM found in the atmosphere. The significant amount of secondary PM is formed in the atmosphere by chemical reactions from the primarily emitted precursors. Secondary PM over a large

area can be formed by emissions of the gaseous pollutants ammonia, oxides of nitrogen and sulfur dioxide from various sources.

The monitoring of particulate lead (Pb) (since around 1985) allowed to understand the dangers of the lead-in petrol and led to the ban on sales of leaded petrol (in 2000) [35]. Despite the ban, around eighteen countries (including Algeria, Yemen, and Iraq) continue using leaded gasoline due to short-sighted economic benefits [36]. The lead exposure includes neurotoxic effects, such as low IQ and antisocial behavior, especially affecting children.

In some countries (for example, UK), the measurement of metals in small particles is based on PM10 fraction. The particles are sampled by taking a known volume of air through a cellulose filter, which is located in a low- or high-volume sampler. The cellulose filter is then dissolved in an acid mixture (HNO3 and H2O2), with following metal analysis by inductively coupled plasma-mass spectrometry (ICP-MS). ICP-MS is a very sensitive technique and is especially suitable for detecting the trace elements. Mainly the concentrations of nickel (Ni), arsenic (As), cadmium (Cd), and lead (Pb) are routinely accessed.

Major ions, especially sulfate anions, are measured similarly. First, the particles are captured on a cellulose acetate filter. Then, after the aqueous extraction, the sample is analyzed by ion chromatography (IC). Some other methods are applied to detect ammonium ions  $(NH^{4+})$  – here flow injection permeation/conductivity measurements are performed.

Polycyclic aromatic hydrocarbons (PAHs) are a class of chemicals, which are nonpolar and lipophilic, posing health risks. The exposure to humans leads to cancer, cardiovascular diseases and have an impact on fetal development. PAHs are routinely monitored due to its toxicity. While PHAs are monitored in the PM15, and PM10 particles, more advanced methods allow monitoring PAHs concentration also in smaller particles. The PAHs are captured in the volatile and non-volatile phases and collected using polyurethane (PU) foam plugs or filter papers. PAHs can be extracted using dichloromethane. The following gas chromatography with the mass spectrometric detection (GC-MS) allows quantification of many individual PAHs (even 32 different formulas). The main PAHs routinely measured are acenaphthene, anthracene, benzanthracene, benzfluoranthracene, benzopyrene, chrysene, fluorene, phenanthrene, and pyrene [37].

#### 4.3. Other PM factors to consider

Besides the PM surface area and the surface chemical composition, there are many known and yet to discover important factors to mention.

### 4.3.1. Particle collective behavior

The smaller particles, especially in large numbers, obey the law of particle physics, which are different for the bulk materials. Especially the nanoparticles (smaller than 1  $\mu$ m) exhibit the collective behavior, and the group of such particles sometimes is denoted as the nanoparticulate matter. The nanomaterials also differ from the bulk materials in surface and quantum effects [38]. The surface area for the small nanoparticles massively increases, with the effect that surface atoms have a different environment to interior atoms. Such size effect is notable for the nanoparticles smaller than ~5 – 50 nm [39]. One can calculate that from several hundred to  $10^5$  atoms are present in one nanoparticle of size 1 or 100 nm. Recent evidence has shown that PM0.1 can aggregate into larger particles about the size of PM2.5 [40].

#### 4.3.2. Particle shape

The particles shape is also of high importance. Asbestos consists of long microscopic fibrils (0.1 – 10  $\mu$ m) with 1:20 aspect ratio. The inhalation of asbestos dust allows the small particles with sharp angles to penetrate and damage lungs. Usually, the higher the aspect ratio, the more toxic is the

asbestos particle [41]. In the case of nanoparticles, these are usually classified to one-, two- or three-dimensional nanomaterials. Asbestos fibers represent 2D-nanoparticles.

## 345 4.3.3. Particle charge

 With the artificial production of various kinds of nanoparticles in the laboratory, we should take into account also the composition (made of a single or from several materials), magnetic and electromagnetic properties. Such properties influence the nanoparticles clustering (agglomeration) when these particle clusters behave as larger particles. Some studies showed the faster diffusion of negatively charged latex nanoparticles across the mucus layer of the gastrointestinal tract, while the positively charged particles were trapped in the negatively charged mucus [42,43].

#### 4.3.4. A particle as a biological and genetic information carrier

The dust particles, including the pollen grains from the male seed plants, are the carrier of genetic (DNA) and biological (such as proteins) information. The human immune system may react to the inhaled pollen by allergic reactions. Mainly the proteins of the pollen surface cause the immune reactions, such as allergy or asthma. The human immune system cross-reacts to a wide range of carriers, the allergens. The same protein, having a similar structure but coming from various sources (such as flees, cat fur, etc.) potentially can cause immune reactions [44-46]. There are attempts to classify the allergens and expressed proteins based on their encoding DNA. More allergens have been identified, with more of the research needed to analyze the effect on human body [47,48]. Metagenomics methods allow collecting the particles in the air over time, extracting the metagenome DNA, with following sequencing of all DNA. The sequencing enables understanding the species (such as bacteria, fungi or other microbes) which "inhibit" or deposits its DNA or proteins on the dust particles [30,49].

### 5. Pollutant toxicity measurement utilizing OoC

The toxicity test for the health and environmental regulations should account for the nanoparticle size, surface reactivity, and possible agglomeration. There are a lot of human-made products that include nano and microparticles: food additives, toothpaste, cosmetics, sunscreens, stain-resistant clothing, tires, etc. While some of the nanoparticles (such as TiO<sub>2</sub> for sunscreen) are standardized and their health effect is known, for other, especially novel particles, extensive toxicity tests should be done until they are allowed to be incorporated into our daily products. Not only the health effects on humans are important, but we should also consider the distribution ways delivering the particles through the tap water to our rivers and oceans, impacting the aqua-living organisms. There is still no simple relationship between the nanoparticle classification (such as dimensionality, morphology, composition or agglomeration state) and health effects. We should mention that not all nanoparticles are toxic – some seem to be non-toxic [50,51], and other find a wide spectrum of applications in the healthcare system [52]. For more detailed studies on health effects of PM and nanoparticles, we recommend recent reviews [53-56].

The development in Organ-on-a-Chip area allows monitoring the growth of mammalian cells over an extended period. By including some chemicals, representing pollution sources, the growth and any abnormalities in cells can be observed. The toxicity (damage to the cells) and the dose can be determined [57]. We envision OoC methodology as the fast, ethically responsible (no animals involved in the research) and available to measure particle toxicity effects for any laboratory equipped with mammalian culture room [30,58].

#### 6. Tracing the source of the pollutant

One of the reasons to detect pollutant and measure their concentrations is to understand what these pollutants are, where do they come from and how to avoid them. Both the chemical (metals, organics, etc.) and biological (species, DNA, proteins, metabolites other molecules) properties can be analyzed, both qualitatively and quantitatively to understand pollution and its source.

Sometimes, even a single chemical or even an elemental tracer can be used as a marker that indicates the origin. For example, sodium (Na) in the pollutant indicates the sea salt as a source, and the presence of aluminum and silicon indicates the soil and crustal dust as an origin. Fuel oil combustion can be detected by the presence of vanadium (V) and nickel (Ni), whereas the vehicle brake wear produces barium (Ba) pollutants. The combination of chemical components allows easier identification and quantification of sources. Of course, various localities have specific pollutant sources, and this should be taken into account.

The biomass burning can be identified by a single marker, the carbohydrate compound levoglucosan [59,60]. Levoglucosan is an organic compound with a six-carbon ring structure formed from the pyrolysis of carbohydrates, such as cellulose. The wood smoke also contains other tracers, such as fine particle potassium (K). However, the potassium produced by the wood smoke should be differentiated from wind-blown soil and sea salt, as well as the road traffic. The wood smoke to fine particle potassium mass ratio depends on wood combustion conditions, and the wood smoke mass is measured by the Aethalometer [61,62]. The quantitative discrimination of carbonaceous particles produced by the wood burning and road traffic emission can be done by utilizing aerosol light absorption measurements [62]. Another, and the most reliable way of estimating wood smoke mass is from the analysis of radiocarbon isotope (14C). This kind of radiocarbon is associated with present-day sources of carbon and not with fossil sources. Heal et al. analyzed PM2.5 samples for the radiocarbon. By thermal separation of elemental carbon from organic, they were able to determine the radiocarbon content of each. Finally, they disaggregated the carbonaceous components of PM2.5 into EC or OC, originating from biomass (such as burning wood or contemporary fuels), fossils (road vehicle engines or coal combustion), and biogenic carbon (from vegetation waste and other biogenic precursors) [63].

The secondary organic matter can be calculated from the excess of OC when the ratio between primary OC and EC is known. While there is still a correction needed, because the analysis of radiocarbon overestimates the OC: EC ratio, the method is advantageous as it allows to distinguish between organic material derived from fossil fuel sources and that from biogenic sources [64]. The work on Yin et al. analyzed the sources of the organic compounds in the atmosphere. The analysis of a large number of organic molecular markers within the PM, such as sterols, organic acids, n-alkanes, hopanes, PAHs, also some trace elements [65] allowed to disaggregate the OC into various source components [66]. Following OC sources could be identified: wood smoke, vegetative detritus (i.e., fragments from plants, such as leaves), suspended dust and soil, particles from diesel, gasoline or smoking engines, also the particles from coal or natural gas combustion.

Organic and biological molecules can be utilized for tracking the pollution sources originating from the food production. Even simple cooking of the meat or corn oil produces a cooking aerosol with unique molecules suitable to serve as the tracers. The peptide mass fingerprinting (PMF) with the aerosol mass spectrometer (AMS) can identify and distinguish unique molecules such as cholesterol or peptides, which are not present in other sources like coal burning or road traffic [66,67].

The life forms and the viruses are the carriers of the coding DNA or RNA. Many of potentially harmful microorganisms attach to the dust particles and are carried over long distances. Metagenomics (DNA sequencing of captured species) allows identifying and tracing such pollutants originating from microorganisms [68]. It is anticipated that not only DNA and RNA analysis can be utilized to trace living organisms, but also the proteins, peptides or other molecules unique to specific species (by mass-spectroscopy or other methods).

#### 7. Summary

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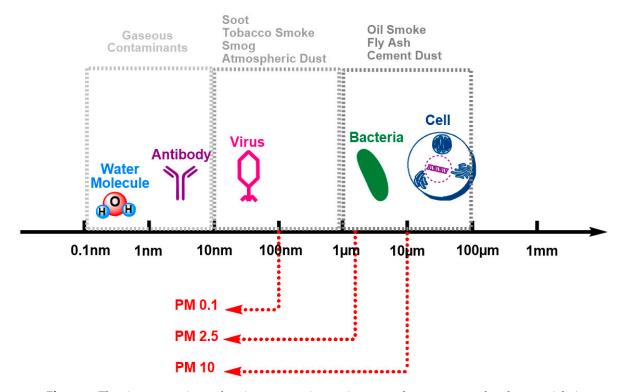
Looking back to the 18th century, with the cities grow and development of the transportation by horses, the main problem was the horse manure (stool), that was accumulating on the city streets and in the open places. The dust from manure is, of course, potentially very health damaging due to various allergens present in the biologicals. Nowadays transportation is based on fuel-powered engines. However, there is a connection between the health effects (such as cancer rates) and how much car engines omit the PM. Despite the requirements to equip the vehicles with diesel particulate filters, and "clean" car manufacturer tests, the situation on the streets look different. In reality, many cities are starting to ban diesel-powered vehicles to enter the city center. Some cities are planning to ban both gasoline- and diesel-powered vehicles. Fortunately, the development of alternatively powered cars is rapidly advancing. Nowadays it is possible to purchase a hybrid or a fully electric car from the most of the car manufacturers. With the development of necessary infrastructure, we can hope our future will look bright. Some problems, however, will have to be solved. How will the non-exhaust emissions be solved? Such as the PM generation from the road itself, from the vehicle tires and brakes, or dust particles on the road. With all of our desire to live in a clean environment, we can anticipate the technological advancements for the tire materials, as well as for the road material. Currently, the PM2.5: PM10 mass fraction is measured to estimate the non-exhaust traffic sources.

Besides the traffic-related pollution, there are other, industry-related PM sources. One can expect the energy source based on the coal and diesel to diminish to the minimum or go away at all. The human is responsible for the anthropogenic pollution sources, and with right policies, this can be handled in the right way, leading to the much cleaner environment, for the benefit of the healthier population. The non-anthropogenic pollution sources, such as dust storms, are much more difficult to control, if at all. However, the monitoring stations, located in each of the city, other locations will help to predict, detect and follow the pollutants. With the advanced technology, the pollutants can be followed from the source, moving over territories and continents. Besides the on-ground meteorological stations, the PM can be monitored utilizing satellites. The satellites are progressively involved in detecting and analyzing not only the particle size but also the pollutant cloud size, the chemistry, even secondary reactions in the atmosphere [69,70]. With the ongoing integration of the data sources, both from the meteorological stations and satellites, we can expect more precise information on the pollutant kind and the toxicity to the population. Informed people can adjust behavior, such as how much time to spend in outside activities, and how much and what kind of protection is needed. That happens right now in developing and developed Asian countries such as Singapore, Hong Kong or China. People can read the air quality values on TV, on the internet, and probably by the fastest way – on the mobile phones.

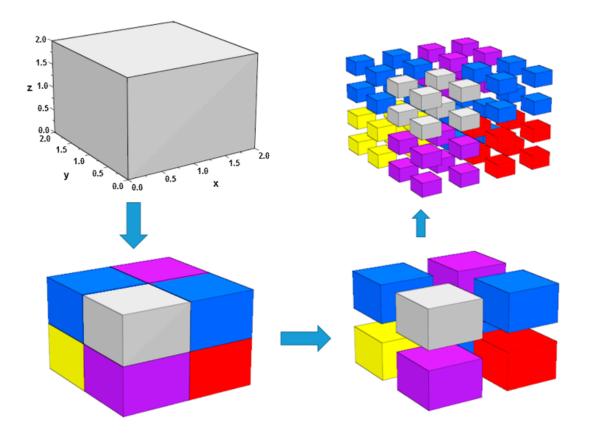
There are different modeling methods for the primary and secondary pollutants, PM concentration, and distribution. The models allow assessing the PM concentration in the locations where monitoring stations are not available and allow to estimate the PM change in the future. Despite the many uncertainties in the data and processes, Pollution Climate Mapping (PMC) [71] and the ADMS-Urban models [72,73] are few of examples worth mentioning.

Ideally, the technologies would help to detect the pollution source as early as possible. With the right policies in place, the pollution can be minimized. To enable the enforcing these policies, an effective and PM detection technology is needed. Overall, the long-term records are necessary to understand the pollution itself, for the delivering suitable policies and actions on the concentration of any given pollutant.

### 492 7. Figures and Table



**Figure 1.** The size comparison of various contaminants (gaseous phase, soot, smoke, dust particles) with the chemical and biological molecules and cells. PM value represents the median value of the particle size for that particular PM (such as PM0.1, PM2.5, and PM10).



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498 Figure 2. When the cube is divided into eight smaller parts, its surface area increases from  $24 m^2$  to 499 the total surface area of 48 m<sup>2</sup>. Further division into 64 parts will result in the total surface area of 96 500

#### **Table 1.** The PM features and relation to the human health.

PM feature	Influence on health
Particle size	Smaller particles penetrate easier and deeper into organs
Chemical composition	Lead (Pb) or PAH cancirogenous particles are especially poisonous
Small particle collective	The effect is not known, could be a cumulative effect, of the small and
behavior	larger particles
Shape	Higher or irregular shape is known to be a more damaging (i.e., asbestos to the lungs)
Charge	Negatively charged nanoparticles may cross more easily the mucus
	layer, comparing to the positively charged particles
Biologics carrier	Proteins similar to allergens may cause immunoreactions

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