

Defining Aerosols by Physical and Chemical Characteristics Shandilya, Kaushik K.^a, Khare, Mukesh^{b*} and Gupta, Akhilendra B.^c

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Abstract

An aerosol is a suspension of fine particles in a gas, usually air, and is generally taken to include both solid and liquid particles with dimensions ranging from a few nanometers up to around 20 micrometers in diameter. This paper presents an overview of the various physical and chemical characteristics of aerosols. It also highlights some gaps in the existing knowledge on aerosols and throws open certain ideas on which research could be initiated.

Keywords: Aerosol, Physical and Chemical Characteristics, Size and shape, Sources, Mechanisms.

1. Introduction

The word aerosol covers a wide range of materials that remain suspended in the atmosphere for a long time. As the suspension takes place in the gaseous medium, the atmosphere can be considered an aerosol in the broadest sense. Usually, however, aerosol refers to small solid and liquid matter in the atmosphere, with subset solid matter often defined as particles or particulates. Aerosols should be distinguished from dust, which is a larger piece of solid material approximately 20 μm diameter or greater that settles out of the atmosphere by suspension and gravitation. The nuclei (<0.1 μm diameter) and accumulation (0.1-2.0 μm diameter) modes comprise the fine particles while particles of size (>2.0 μm diameter) constitute the coarse mode. Vehicular exhausts are major sources of fine particles in the atmosphere (Shandilya, 2002a).

Chemical composition of particulates in the atmosphere varies. These particulates can be homogeneous or heterogeneous in their structures. Atmospheric particulates contain both organic and inorganic components. Inorganic components or elements may be derived from both, natural or manmade sources. Aerosols may also consist of organic constituents.

Particles in the range of visible light (0.38-0.76 μm) are most effective in visibility reduction. Five to 20 percent of Suspended Particulate Matter (SPM) involved in light scattering contains sulfates and sulfuric acid mist. Sulfur dioxide concentrations of 26 $\mu\text{g}/\text{m}^3$, humidity of 50 percent, will reduce visibility to eight km. Decreased visibility of this severity interferes with safe operation of aircraft and automobiles. At least 15 to 20 plane crashes are attributed to poor visibility caused by smoke, dust and haze.

Aerosols can be transported over long distances affecting air quality and climate on a global scale. They can also be used as tracers of meteorological changes, such as inversion heights, inversion strengths, location and depth of stable layers (Prospero et al, 1983; Heintzenberg, 1989). Aerosol measurements can also be used as tracers to study how the Earth's atmosphere moves. Because aerosols change their characteristics very slowly, they are much better tracers for atmospheric motions than chemical species. Aerosols have been used to study the dynamics of Polar Regions, stratospheric transport from low to high latitudes and air exchange between troposphere and stratosphere.

There are thousands of detectable compounds in the atmospheric air, however, our knowledge is sufficiently limited to preclude assessment of their contribution to observed atmospheric phenomena. In general, aerosol particles are an important part of the life cycle of many such chemical substances. The study of one such element, sulfur, enables one to see this clearly. There is growing awareness of the role of sulfur compounds in determining the characteristics of aerosol and sufficient data do exist on sulfur for it to serve as an example.

In total aerosol budgets, majority of sulfur data are given as global averages. Since approximately 30-50 percent of the atmospheric sulfur is anthropogenic and since humans populate only a small percentage of the earth, the role of sulfur compounds in the atmosphere can only be understood by studying its local or regional sulfur cycles. Although,

quantitative data are so far lacking, man may dominate the regional cycles in the world. Atmospheric S exists largely in such reduced forms as hydrogen sulfide, methyl sulfide, etc., and in the oxidized forms of sulfur dioxide and sulfate ions by a variety of gas phase and liquid surface reactions (Stern, 1977).

2. Sources of Aerosols

Aerosols originate from two main source regions. Primary aerosols directly injected in to the atmosphere from the earth's surface often come from the volcanoes, forest fires, re-suspension of soil material in rural areas, biological sources (pollen, bacteria, fungi), meteoric debris, the ocean surface and the anthropogenic process. Almost 90 percent of these particulate emissions occur in the troposphere.

Figure I shows the schematic diagram of input to the atmosphere from different sources. These aerosols penetrate the atmosphere in many sizes. A general classification often used is a division at about two micrometers. The definition varies somewhat according to the size range of the aerosols to be measured and the method.

Secondary aerosols are formed after chemical conversion in the atmosphere involving gases, other aerosols and atmospheric components, particularly the moisture. Unfortunately, the details about the chemistry of trace gases to aerosol conversion are still limited. Table 1 lists the various transformation processes and sources of fine particulates.

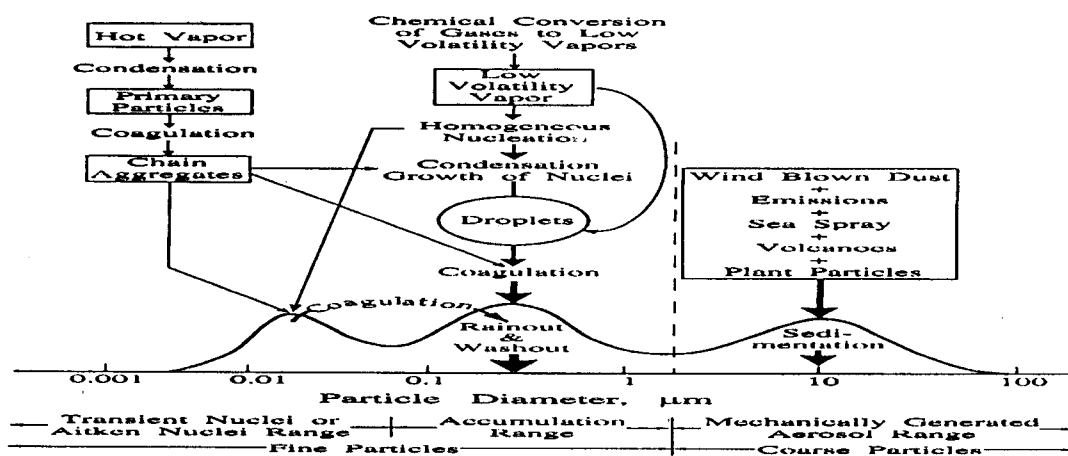


Figure I: Schematic of the Aerosol sources and the affecting processes in the atmosphere (<http://cloudbase.phy.umist.ac.uk/people/dorsey/Image2.gif>)

Table I: Transformation Processes and Sources of Fine Particles

Transformation Process	Sources
Primary Particles	Anthropogenic fuel combustion, road transport, industrial processes, domestic burning, wood combustion, Sea salt and soil dust.
Secondary particles	
SO ₄ ²⁻	Oxidation of SO ₂
NH ₄ ⁺	Fossil fuel combustion, volcanic emissions
NO ₃	Oxidation of NO _x fossil fuel combustion, vehicle exhaust, Reduction of NH ₃ animals, sewage, motor vehicles
Elemental C	Motor vehicle exhaust, wood burning.
Organic C	Oxidation of chemical use, vegetation, motor vehicles

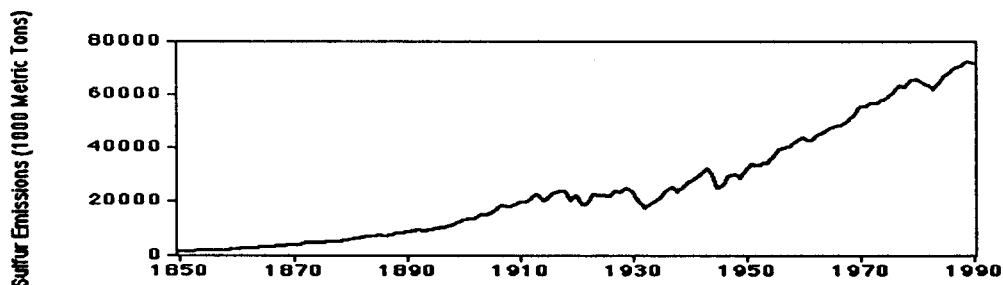
Major organic species and hydrocarbons (HC) which form a sizeable fraction of the atmospheric aerosols are Benzene Soluble Fraction (BSF), Peroxy Acetyl Nitrate (PAN), Total Volatile Matter (TVM), Total Carbon (TC), Total Organic Carbon (TOC) and Elemental Carbon (EC). Most of these species are the result of combustion processes. Methane is an exceptional HC that occurs naturally. Acidic aerosols trace mainly to the combustion of sulfur-containing fossil fuels and reactions of the photochemical free radicals with the nitrogen dioxide. This is tricky mainly for the PM₁₀ coarse fraction.

Aerosols other than particulate matter are also present in the atmosphere. They play an important role in aerosol atmospheric chemistry and physics. Important aerosols are described here as under:

2.1 Sulfur Oxides Emission

The long-term historical trend in SO₂ emissions is summarized in Figure II. It may be seen

Estimates of Global Sulfur Emissions



SOURCE: A.S.L. & ASSOCIATES, HELENA MT

Figure II: Global historical trend of SO₂ emission (<http://www.asl-associates.com/globals.htm>)

from the plot that from 1860 to 1965, SO₂ emissions have increased 28-fold. From 1860-1910, they doubled every 16 years. The exponential rate slowed but the absolute rate continued to rise leaving aside the period from 1920-1930. The very last double-up took place in 1940-1965.

2.2 Nitrogen Oxides Emission

Roughly 500×10^6 tons of NO is emitted worldwide each year from natural sources, practically the bacterial action. Manmade sources of NO and NO₂ account for another 53×10^6 tons/yr of NO_x (computed as NO₂). From this flux and the worldwide average ambient average concentration of 7.5×10^{10} molecules/cm³ (3×10^{-3} ppm) of NO_x, the lifetime for NO_x is found to be about nine days. On a global scale, the manmade contribution is significant but not dominant. The flux of 4.1×10^{10} molecules/cm²-sec for NO+NO₂ calculated from worldwide emissions is offset by the downward flow of HNO₃ from the stratosphere.

Almost half of NO_x emissions are from coal combustion, with petroleum product combustion being almost as large. US accounts for almost 40 percent of world emissions. NO_x is one of the main ingredients that gets involved in the formation of ground-level O₃ (Ozone is formed when NO_x and VOCs react in the presence of heat and sunlight), reacts to form NO₃ particles, acid aerosols, as well as NO₂, contributes to the formation of acid rain, contributes to the nutrient overload that deteriorates water quality, contributes to atmospheric particles, which cause the visibility impairment most noticeable in the National parks and reacts to form toxic chemicals.

2.3 Organic Matter

Important component of organic matter in aerosols is polycyclic aromatic hydrocarbons which are considered as highly toxic. At present, the exact mechanism of polycyclic

aromatic hydrocarbon formation during combustion is not understood in detail. Three different pyrolysis mechanisms are currently considered as possible; Slow Diels-Alder condensations, Rapid radical reactions, and Ionic reaction mechanisms.

3. Physical Properties of Fine Particulates

Particle physical characteristics are generally characterized under the microscope either by light microscope or by scanning electron microscope (Shandilya, 2002a, Shandilya 2008a, 2008b). The crystallography is carried out by X-ray diffraction meter (Shandilya, 2008a, 2008b). Various characteristics related to particulates are as follows.

3.1: Particle Size

Particles smaller than 40µm do not tend to settle rapidly, called as suspended particulate matter (SPM). Metallurgical fumes, cement dust, fly ash, carbon black and sulfuric acid mist fall into the 0.01-100µm range. Mists are typically less than 10µm in diameter. A typical size distribution according to the components present can be given as Figure III. It may be seen that there is no sharp cut-off between the classifications. The particle sizes in each class overlap into the neighbouring class. This may be due to several factors that tend to make proper collection and classification of the particles difficult and somewhat inexact.

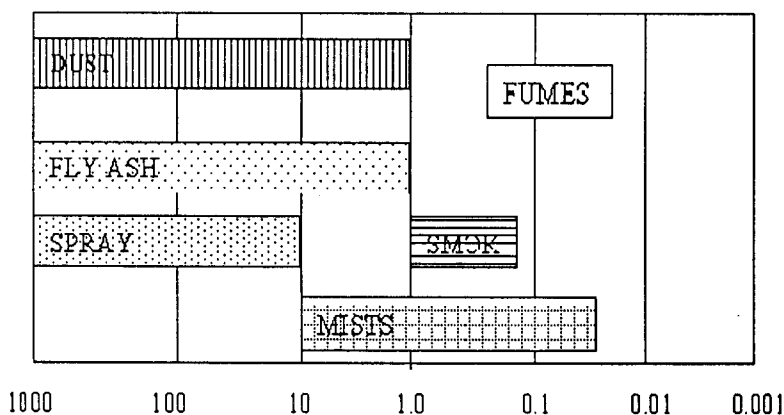


FIG III: Size distribution of particles in ambient air (Chow, J. C., 1995).

Superimposed on this figure are the size ranges of particles deposited in the respiratory tract of man and those associated with the two sampling methods accepted in the air pollution field for evaluation of particulate matter in the urban atmosphere, i.e., dust fall jar and SPM evaluation by high-volume Sampler. The nomenclature of the natural aerosols and the importance of the particle size for the various atmospheric phenomena is thus in terms of the deposition of the particles in the upper and lower respiratory tract after inhalation by man. The above nomenclature is used by many meteorologists and cloud physicists to describe atmospheric particles.

Urban and natural aerosols are poly-disperse with respect to particle size, encompassing size range from approximately 6×10^{-4} to $10^3 \mu\text{m}$. Because the effects produced by the aerosols are associated with concentrations of particles in selected ranges of size spectrum, knowledge of particle size distribution in polluted and non polluted atmosphere is essential for understanding aerosol phenomena occurring there. What makes aerosol research unique, however, is that most of the mass changing processes depend on the particle size. Size and the size distribution of the atmospheric aerosols affect both the chemical and the adhesive properties of the particles.

Particles less than 0.1 to $0.2 \mu\text{m}$ do not move in response to gravitation or electrostatic forces, but are controlled by the Brownian motion. Diffusion processes direct the deposition rates of these small particles. The deposition of the larger particles is,

however, determined by the aerodynamic processes such as impaction with precipitation or sedimentation to ground.

3.2: Ambient Particle Size Distributions

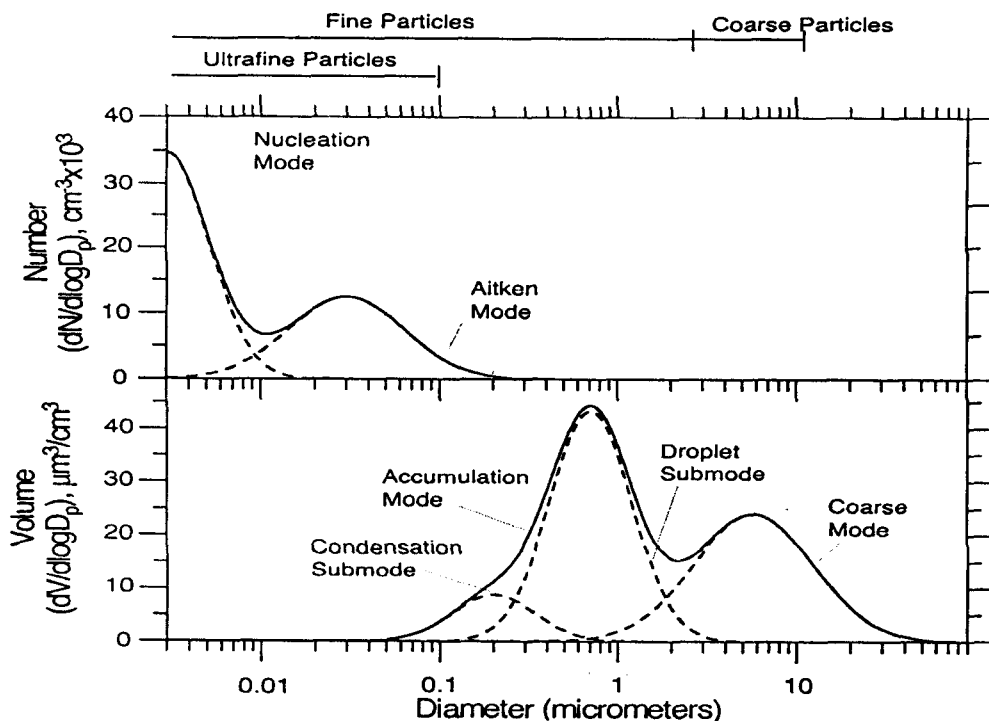


Figure IV: Number and Volume distribution of particle sizes

Fig IV shows a typical number and volume of the particle sizes found in the atmosphere (http://www.epa.gov/r10earth/psgb/media/pdf/images/airshed_characterization_img_21.jpg). It may be seen that mass collected is proportional to the area under distribution within each size range. When sampled, each of these size ranges contains a certain abundance of the particles above upper size designation of each range (Watson et al, 1994; Wedding and Carney, 1983). There is no sharp cut-off between the classifications, and the particle sizes in each class overlap in the neighbouring class. Established size fractions are the ultra fine particles (diameter <0.1 μm), the fine fraction of PM₁₀ with PM_{2.5} and the coarse fraction of PM₁₀ PM_{10-2.5}. There may be slight overlap but the fine and coarse modes have distinct origins, elemental distribution and the residence time and the removal processes.

3.3: Modes

Observations of the high ultra-fine particle (3nm<Dp<20 nm) number concentrations in the clean upper tropospheric air and the process-model calculations suggest that this region may be a source of new nuclei (Raes et al., 1997). Air in cumulus updrafts may be scavenged of nearly all its aerosol mass, resulting in an air mass with low particle surface area. In addition, low temperatures at these altitudes reduce saturation vapor pressures, thus promoting bursts of nucleation, followed by coagulation. Subsidence and entrainment can then bring these fresh nuclei into the boundary layer.

The particle number size distribution is a measurements' fundamental physical property required for gas-phase understanding of the evolution and the gas/particle partitioning of the ambient aerosol. Typical particle number size distributions are shown in the Figure V.

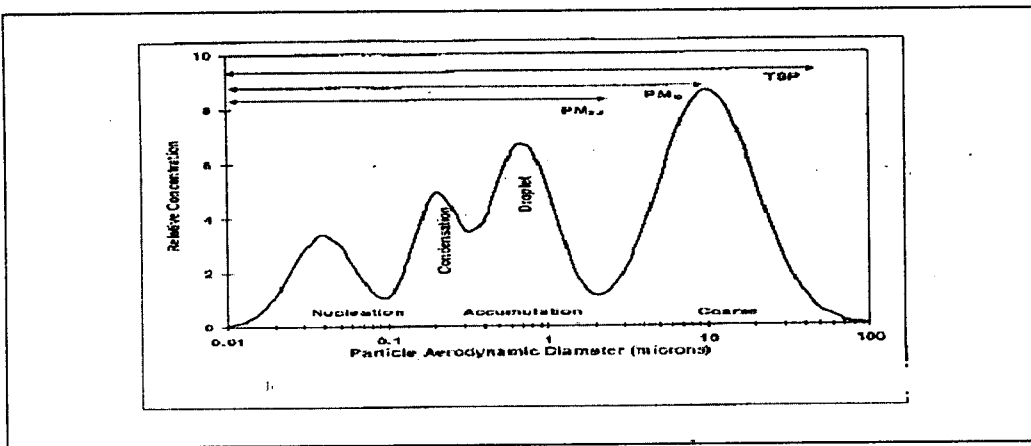


Figure V: Idealized size distribution of particles in ambient air (Chow et al., 1995)

3.4: Condensation Nuclei

The smallest particles are formed by condensation of vapours or by photochemical nucleation. These particles are less than $0.1\mu\text{m}$. Figure VI shows the typical particle size - mass fraction diagram for particulate matter in urban air (<http://www.cpcb.nic.in/oldwebsite/Highlights/Highlights05/image/Image3570.gif>).

The “nucleation” range, also termed “ultra fine particles” with diameters less than $0.08\mu\text{m}$, are emitted either directly from combustion sources or are formed by condensation from cooled gases soon after emission. Sometimes called Aitken Nuclei, these are small particles that act as condensation sites for the super saturated vapours in the atmosphere. The lifetimes of the particles in the nucleation range are usually less than one hour because they rapidly coagulate with larger particles or serve as nuclei for the cloud or the fog droplets. This size range is detected only when fresh emission sources are close to a measurement site or when new particles have been recently formed in the atmosphere (Chow, 1995). Aitken nuclei mode ($<0.1\mu\text{m}$) accounts for most of the particles by the number. Coagulation processes convert these nuclei into the large size particles ($\text{PM}_{0.1}$).

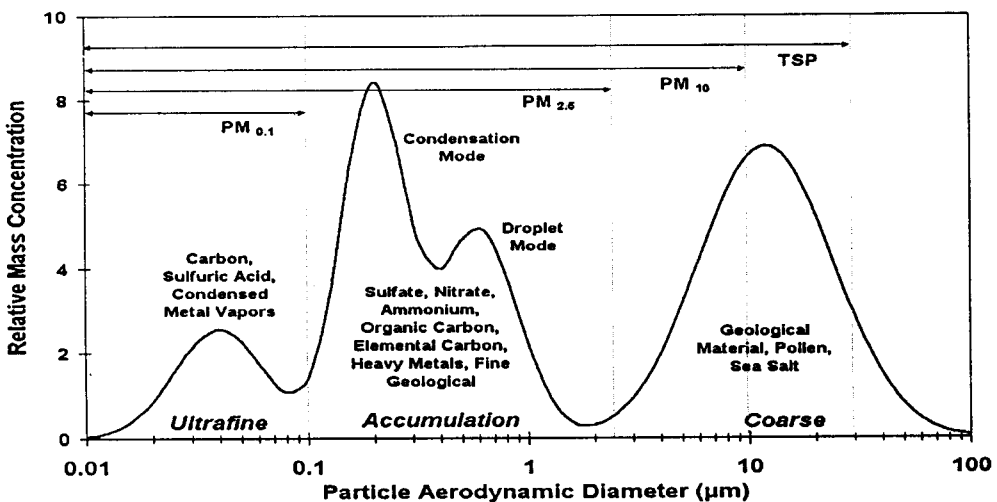


Figure VI: A typical particle size-mass fraction diagram for particulate matter in urban air

3.5: Accumulation Range

Particles that are composed of several smaller particles are attached to the large particles or to each other and travel together in the atmosphere as a single particle. The number size

distribution is usually best fit by the sum of two lognormal modes, an Aitken, and an accumulation mode (<http://www.faqs.org/>). Accumulation mode (0.1-2.5 μm) accounts for about 33 percent to 50 percent of the particle volume and the mass. Accumulation mode and the nuclei mode are collectively termed as the fine mode (<2.5 μm) PM_{2.5}. The coarse mode (>2.5 μm) contains small number of the particles and about 1/2 to 2/3 of the particle volume and the mass. The schematic diagram of an atmospheric aerosol surface area distribution showing principal modes, main sources of mass for each mode, and the principal process involved in inserting mass in each mode and the principal removal mechanisms is shown in Figure VII.

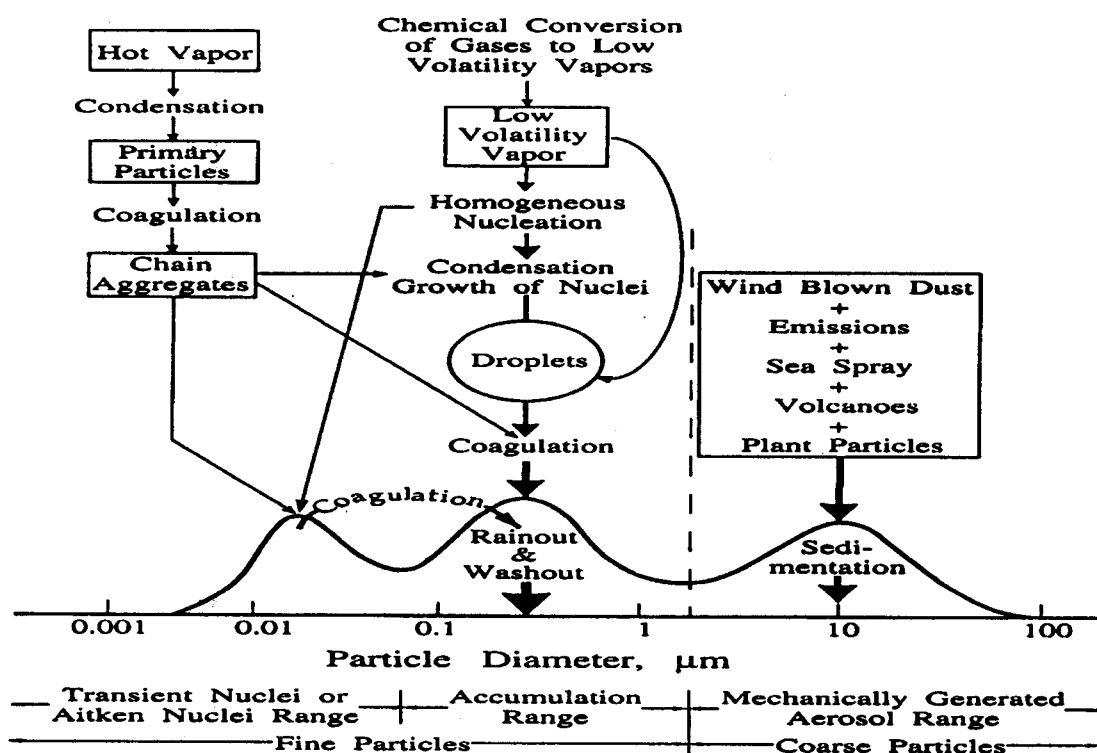


Figure VII: Schematic diagram of atmospheric aerosol surface area distribution (se.phy.umist.ac.uk/people/dorsey/Image2.gif)

3.6: Agglomerates

Agglomerates are particles that are composed of several smaller particles attached to a large particle or to each other and travel together in the atmosphere as a single particle. Although most particles are in the nucleation mode, the particles in the accumulation mode account for the largest portion of the surface area. The agglomeration of the nuclei onto the particles in the accumulation mode reduces the number of the nuclei by 79 percent per hour. The agglomeration of the nuclei with themselves reduces their number by 31 percent per hour (Stern, 1977). The fine particles agglomerate with themselves, but do not transfer to the coarse particulate mode.

3.7: Coagulation

Based on the direct microscopic observations of the morphology and the composition of the urban particles, Whytlaw-Gray and Patterson (1932) proposed that coagulation should be an important mechanism shaping the size distribution of the atmospheric aerosols. Later, Junge (1952) also concluded that the balance between the sources and the coagulation decay of the particles determines the lower end of the aerosol size distribution, below 1.0 μm . The larger

particles fall out rapidly and the moderate sized ones more slowly. The settling velocity of unit density spheres in still air is as listed in Table II (<http://www.cs.ruu.nl/wais/html/nadir/ozone-depletion/.html>).

Table II: Settling Velocity of unit density sphere in still air

Particle Diameter (µm)	Settling Velocity, Vs (cm/s)
1000	385
500	200
220	76
100	25.1
50	7.2
40	4.8
30	2.7
10	0.3
1	0.0035

3.8: Sedimentation

The Peak of the coarse mode may shift between six and 25µm. A small shift in the 50 percent cut-point of a PM₁₀ sampler will have a large influence on the mass collected, because the coarse mode usually peaks near 10µm. On the other hand, a similar shift in the cut-point near 2.5 µm will have a small effect on the mass collected, owing to the low quantities of the particles in the one to three µm size range. Coarse particles are formed by the mechanical processes such as grinding and evaporation of the liquid droplets. Urban aerosols usually show a bimodal mass distribution with a maximum around 0.2-0.3µm for coagulation mode and a maximum around eight µm for sedimentation mode. Here, the coagulation mode and the sedimentation mode did not have distinct maxima. This shows the distinction between the coagulation mode and the sedimentation mode particles reported in the literature (<http://www.lib.ox.ac.uk/>).

3.9: Fundamental Approach

It is essential to consider the dependence of the particle properties on the particle size when setting out to describe the atmospheric aerosol. In a poly-disperse urban aerosol the distribution of r^2 must be determined, which is the frequency distribution curve of the second moment. Thus, the fraction of total number of the particles in the size range between r and $r+dr$ is given by

$$dn=f\{r\} dr$$

with the condition that

$$\int_{\infty}^0 f(r) dr=1$$

The two mathematical models, which have been frequently used to describe the particle size distribution of the atmospheric aerosol, are the logarithmic normal and the log radius particle count, area, or the weight distributions. The log radius number distribution is defined by

$$n(r)=dN/(d\log r) \text{ cm}^{-3}$$

where N is the total concentration (number per cubic centimeter) of the aerosol particles of the radius smaller than r . The number of the particles ΔN between the limits of the interval $\Delta \log r$ can be obtained from a plot of $n(r)$ vs. $\log r$ as follows:

$$\Delta N=n(r) \Delta \log r$$

In addition to particle size data, atmospheric dust fall and concentrations of the gaseous pollutants measured at a sampling site have also been found to adhere closely to a log-normal distribution (Stern, 1977).

3.10: Biological Characteristics

Biological Characteristics are determined in terms of biological species present in the air e.g. pollen, fungi or bacteria. These are shown in figure VIII along with specification of particle size (<http://www.abatement.com/images/airduct/particlesize.gif>).

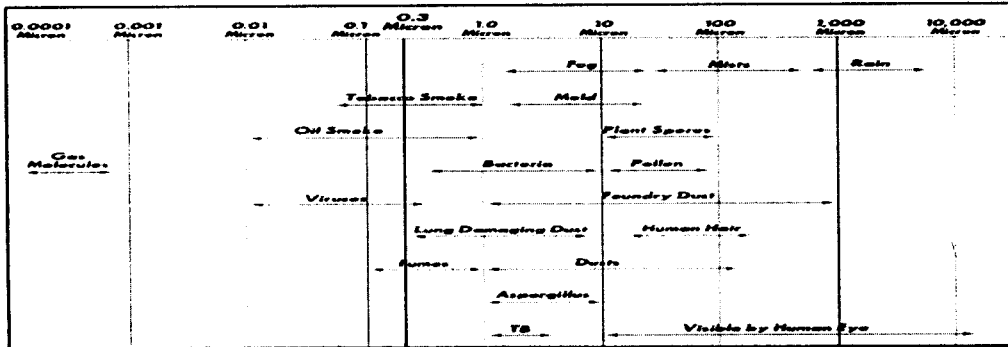


Figure VIII: Bio-aerosols and their particle size distribution

4. Particle Shape

Particle shape or certain morphological features (morphology relates to the particle shape and surface features) such as porosity and roughness, are of great significance in characterizing the effect of the particles on health and their role in the atmospheric reactions. The shape of the particles in an atmospheric aerosol sample will depend upon the local emission sources of the particles.

Morphology of aerosols has not been adequately studied. There are great differences in the shapes of atmospheric particles, which, for the purpose of simplification, can be divided into spherical, irregular, cubical, flake, fibrous, and condensation flocks. Spherical particles include pollen and condensation solids, i.e., fly ash. In this category fibers of wool, cotton, glass, asbestos, and a variety of the synthetic materials can also be found. Minerals are generally geometrically irregular or flake like. Agglomerates can result from particles combining while airborne or can be formed during cooling or in hot gases. The latter are characterized by a chainlike appearance and are called flocks. They often are formed during incomplete combustion of fuels and contain a large amount of carbon. The shapes of a few of the particulates are discussed in the following.

4.1: Coal and Coal Fly Ash

Typical fly ash looks like a mixture of geometrically amorphous, but surprisingly characteristic, particles whose approximate shape, particle diameter, and the relative degree of the agglomeration permit quite reliable optical identification. When coal burns, the heat generated may vaporize the material that can subsequently condense to produce fine particles that are called the soot. These range in size from less than 0.1 to 10.0 μ m in diameter.

4.2: Combustion-related Particulates

Incineration of the refuse produces very heterogeneous particulates. The material incinerated largely determines the characteristics of emission, although there are similarities in the particulate collected from a municipal sewage incinerator and from a refuse incinerator.

4.3: Airborne Fibers

In general, synthetic fibers exhibit a smoother and more uniform surface than do plant fibers without flat side appearance of the plant fibers and without traces of the cell structure. Wood fibers may also carry traces of sap or resin.

4.4: Domestic Fires

Typical fly ash from domestic sources consists of small un-fused particles, mostly colourless or white but with some pale yellow material. In addition, there may be small black and red Fe oxide particles (<http://www.cis.ohio-state.edu>).

5. Chemical Characterization of Aerosols

Although emission sources of fine particulates are generally known, knowledge about their chemical composition is still inadequate. Chemical composition helps in understanding chemical reactions occurring in the atmosphere. Most of the reactants of the chemical reactions taking place in the atmosphere are emitted to the atmosphere as *gaseous pollutants*. The importance of sulfur and nitrogen in the formation of fine particulates and their harmful effect especially of fine sulfate particles on human health has stimulated research on the chemistry of aerosol sulfates and nitrates. Many important chemical properties of particulate matter owe their origin to the molecular atomic character.

SO₂ oxidation plays an especially important role in the nucleation of fine particulates. The oxidation process has been determined and includes the creation of SO₃ and its subsequent hydrolysis to form sulfuric acid. Although humidity does not appear to influence the rate of SO₂ oxidation, it does play a dominant role in determining the number of particles formed. In the polluted atmospheres, as many as six million nuclei per cubic centimeter can be formed in an hour. Measurements of SO₂ atmospheric fate have been made, which indicate that SO₂ is converted to particulate sulfate at two percent per hour. Total gaseous sulfur is removed by dry deposition at the rate of 10-20 percent per hour (Stern, 1977). The profile for fine particulate matter is given in Table III.

Table III: Fine Particles Profile

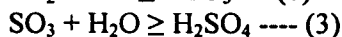
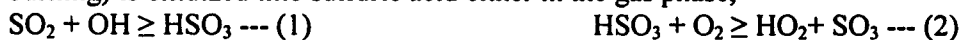
Formation processes	Chemical reaction, nucleation, condensation, coagulation, evaporation of fog and clouds droplets in which gases have dissolved and reacted
Composition	Sulfate, nitrate, ammonium, hydrogen ion, elemental C, organic compounds, PAN, Pb, Cd, V, Ni, Cu, Zn. Particles-bound water and biogenic organics.
Solubility	Largely soluble, hygroscopic and deliquescent.
Sources	Combustion of coal, oil, gasoline, diesel, wood, atmospheric transformation products of NO _x , SO ₂ and organics including biogenic organics, Such as terpenes; high-temperature processes, smelters and steel mills.
Lifetime	Days.
Travel distance	Hundreds of kilometers.
Importance	The chemical composition of the aerosols affects: Toxicity, Water Solubility, Hygroscopicity or The Lack Of It, Deliquescence and Efflorescence, Refractive Index, Particle Shape/State, Acidity related to Acid Rain and Basicity.

6. Chemistry of Oxides of Sulfur and Nitrogen

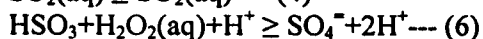
Relatively stable in atmosphere, SO₂ can both reduce and oxidize. Reacting photo-chemically or catalytically with other components in the atmosphere, SO₂ can produce SO₃,

H₂SO₄ droplets and H₂SO₄ salt. SO₂ can also react with water to form sulfurous acid, a weak acid that can react directly with organic dyes. This property is used to detect SO₂ calorimetrically in the atmosphere (Peavy et al, 1985). The transformation of SO₂ to sulfate particles in the Indian atmosphere has been established and modeled by Sharma et al. (2003, 2004).

Sulfur dioxide (SO₂) which is produced either by oxidation of reduced sulfur compounds (e.g., biogenic DMS) or by direct emissions (associated mainly with fossil fuel burning) is oxidized into sulfuric acid either in the gas phase,

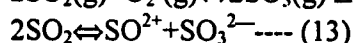
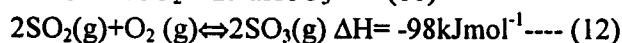
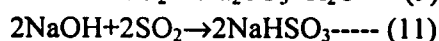
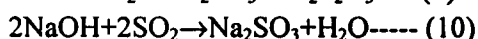
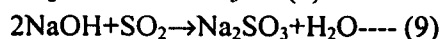
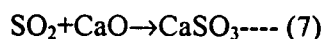


or in aqueous droplets through reactions involving dissolved H₂O₂, O₃ and various transition metal ions, like:

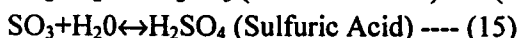


Overall, sulfur dioxide slowly becomes oxidized and hydrolyzed to form sulfuric acid. The oxidation rate tends to limit the acid formation process. Oxidation can occur either in the gas phase or in a condensed phase within the water drops. The gas phase oxidation tends to be slow and, in the absence of the catalysis or highly reactive species (OH, HO₂ or RO₂, O₃), it does not occur at a significant rate (Scott, 1978). This water drop reaction is catalyzed by the presence of certain trace compounds (Freiberg, 1975), provided pH is above 5. At higher pH, oxidation occurs at a significant rate without the presence of catalysts (Scott, 1978). Sulfate formation rates are extremely small except for high pH (Beilke and Gravenhorst, 1978). Oxidation of sulfite ion apparently limits the oxidation rate; resulting in the concentration of this ion to be very small at low pH. Sulfate production rate is quenched as the system becomes more acidic (Scott, 1978).

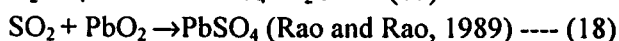
Due to its oxidative property, SO₂ oxidizes the alkali and the alkaline earth metals and reduced itself to SO₃ as follows:



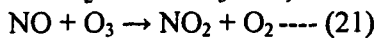
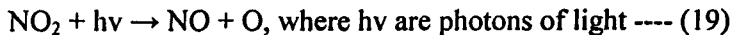
SO₃ is a powerful oxidizing agent, especially when hot. Excess of O₂ and removal of SO₃ from the reaction mixture favours the formation of SO₃. Atmospheric SO₃ residence is dependent on: a) Amount of Moisture, b) Catalytic Particulate Matter, c) Amount of Sunlight, and d) Amount of Precipitation:



Sulfuric acid when it reacts with alkali or alkaline earth metal oxides transforms into sulfates:

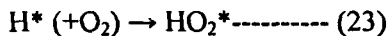


Inorganic nitrogen cycle establishes a relationship among NO, NO₂, and O₃ and also provides major pathways for transforming HO₂ radicals to OH radicals. The primary relationship of NO, NO₂, and O₃ is illustrated by



These reactions interact with hydrocarbon oxidation cycle via reaction of OH and O₃ with hydrocarbons with the resultant formation of HO₂ radicals and oxygenated hydrocarbons. The HO₂ radicals formed then interact with the inorganic cycle via equation (22).

HO₂ is formed from H because of the very fast reaction of H with molecular O₂ as follows:

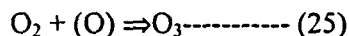


The HO₂* may participate in NO → NO₂ oxidation process, resulting in the accumulation of NO₂ and O₃.

Of the greatest interest in air pollution chemistry of nitrogen oxides are the gas-phase reactions of nitrogen oxides and particularly of NO, which reacts rapidly with ozone to form NO₂. This cycle actually begins when some NO₂ present in the atmosphere absorbs sunlight energy to yield the nascent oxygen, a very powerful oxidizing agent.

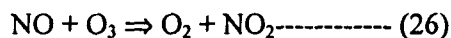


The reaction then continues to produce ozone

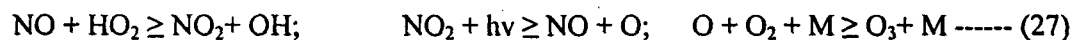


Or intermediate hydrocarbon- oxygen species.

Finally, the reaction terminates with the reformation of NO₂:

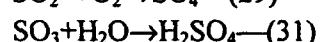
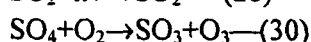
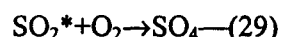
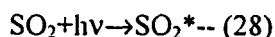


Ozone formation through chemical reactions in the atmosphere is another important phenomenon for tropospheric chemistry. As noted by Crutzen (2000) and Chameides and Walker (1973), the conversion of nitric oxide NO to nitrogen dioxide (NO₂) by Peroxy radicals (HO₂, CH₃O₂, etc.) leads to the formation of ozone during daytime as follows:



Because of the ubiquitous presence of CO, CH₄ and other hydrocarbons plus the short lifetime of NO_x, Ozone production rate is "NO_x-limited" (i.e., O₃ production rate varies primarily with the concentration of NO_x). An understanding of the global and regional budgets of nitrogen oxides, specifically of the anthropogenic versus natural sources of atmospheric NO is crucial to characterize ozone budget in the troposphere.

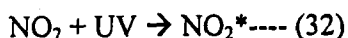
Ozone may be created in the atmosphere as a derivative through photochemical oxidation of SO₂ to H₂SO₄. The reaction takes place as follows:



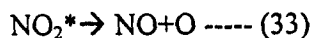
The quantum efficiency for this process is low (Rao and Rao, 1989).

The nature of photochemical reactions in the atmosphere depends on such factors as light intensity, hydrocarbon reactivity and hydrocarbon ratio to nitric oxide, presence of light absorbers and meteorological variables (inversion base and smog are inversely proportional). Nitrogen Dioxide Photochemical Reaction takes place as follows:

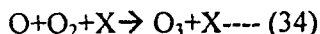
In the beginning, ultraviolet light energy is absorbed by NO₂



The highly energized molecule (NO₂^{*}) then decomposes into the nitric oxide and atomic oxygen.



The atomic oxygen reacts quickly with the molecular oxygen to form O₃. However, this ozone will decompose rapidly unless some other energy is absorbed to form a molecule. In the presence of a third body (X), a stable ozone molecule is formed:



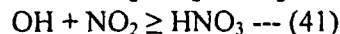
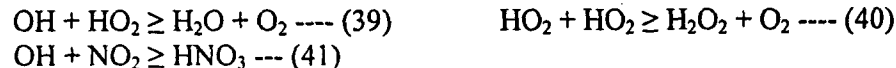
Tropospheric ozone is destroyed by photolysis in ultraviolet and the resulting electronically excited oxygen atom O (1 D) reacts with water vapor:



Hydroxyl radicals OH which are produced by reaction (2) as well as by hydro-peroxyl radicals provide other ozone destruction mechanisms:

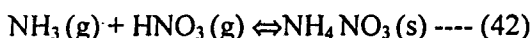


Reaction (2) provides a major source of HO_x (OH and HO₂) radicals while reactions (1), (3), (4) determine partitioning between OH and HO₂. The destruction of these radicals' results from reactions involving OH, HO₂, and NO₂, leading to the formation and the potential wet scavenging of water, hydrogen peroxide and nitric acid:



Oxidation in the atmosphere produces proton and alkaline particles, NH₃ etc. The dissolution of atmospheric NH₃ and the role of alkaline particles remove excess protons, remaining an effective but indirect 'catalyst' for sulfate production.

Formation of solid NH₄NO₃ from the gas phase precursors is described by the equilibrium system as follows:



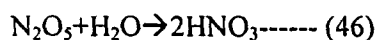
The postulated mechanisms for the loss of nitrate are based on interaction of a strong acid (i.e., H₂SO₄) with NH₄NO₃ or NaNO₃ in the aerosol deposit to form volatile HNO₃ according to the following scheme:



The nitric acid gets formed via:



In the presence of water vapor, the following reaction can take place with oxides of nitrogen:

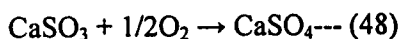


At temperatures $>30^{\circ}\text{C}$, most nitrate is in the gas phase as HNO_3 while at temperatures $<15^{\circ}\text{C}$, most NO_3 will be in the particle phase as NH_4NO_3 , and that there will be varying amounts of HNO_3 and NH_4NO_3 for the intermediate temperature. Relative humidity and concentrations of NH_3 and HNO_3 gases also affect this equilibrium, but temperature is by far the most important variable. When the temperature of air changes during sampling, some of the NH_4NO_3 already collected on the filter can volatilize (Ansari and Pandis, 2000).

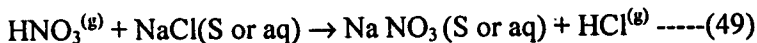
Further, dust particles may be important nuclei for heterogeneous chemical reactions (Dentener et al., 1996); however, NO_x is implicated as the precursor of nitrates and ozone. Thus SO_2 and NO_x transform to sulfates and nitrates in the atmosphere, and become an SPM component. Nitrates and Sulfates are component mixtures with different properties like acidity. The detailed composition of these secondary aerosols depends on the local concentration of NH_3 which neutralizes sulfuric and nitric acid to form NH_4HSO_4 , $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 .

The primary air pollutants causing damage to stone are sulfur compounds, however, a comprehensive decay mechanism must include the roles of nitrogen compounds, carbon dioxide and water. For the carbonate stone-sulfur compound system, general modes of attack include:

Gaseous SO_2



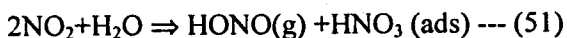
Anhydrous CaSO_4 hydrates form gypsum, which is highly susceptible to surface erosion. A similar reaction of the gaseous nitric acid with sodium chloride in the air leaving sodium nitrate in particle phase (Seinfeld, 1986) is:



Nitrous acid (HONO) also plays a vital function in atmospheric chemistry. It presents an important source of tropospheric OH radicals ($<390\text{nm}$) due to its rapid photolysis:



HONO is formed in a non-catalytic NO_2 reaction of on-soot surfaces, which could represent an atmospheric HONO source:



In the above reaction, NO_2 behaves like a catalyst. When certain hydrocarbons are present, other reactions take place. Some atomic oxygen, ozone and nitric oxide react with hydrocarbons to form various products and intermediates for further reactions.

The rate coefficients for these reactions have not been identified but are presumably equal i.e., at equal concentrations of NO and SO_2 , the NO_2 production rate would be equal to SO_3 production rate. The sum of these rates would equal the NO to NO_2 conversion rate in the absence of SO_2 . This conclusion would only be true for that fraction of the chain carried through RO_2 , HO_2 , radicals, i.e., in the early stages of the olefin catalyzed conversion of NO to NO_2 . In the later stages, HO_2 plays a more important role.

Peroxy radicals are also provided in the atmosphere by oxidation of carbon monoxide, methane and non-methane hydrocarbons by OH as follows:



Further CH_3O_2 oxidation leads to the formation of formaldehyde (H_2CO), and photolysis produces additional HO_2 radicals.

7. Effects of Aerosols

Aerosols affect the planet earth and every living being on it. Aerosols are now recognized as central to such diverse environmental problems as climate change (IPCC, 1995), visibility impairment (NAPAP, 1991) and the eutrophication of remote areas. Aerosols also serve as the sites on which heterogeneous reactions of gaseous trace constituents occur. Among the many pollutants implicated in health effects, particular attention has been focused on fine particulates (Schwartz, 1991; Dockery and Pope, 1994; Pope et al., 1995a; Pope et al., 1995b; Janssen et al., 1997; Wordley et al., 1997) and PAHs.

Aerosols interact both directly and indirectly with Earth's radiation budget. Aerosols scatter sunlight directly back into the space. Indirectly, low-atmospheric aerosols can modify cloud particle size which affect Earth's energy budget. Aerosols also can act as the sites for chemical reactions to take place (heterogeneous chemistry). The most important heterogeneous reactions are those that lead to the damage of stratospheric ozone. In the following we discuss some of the major effects point wise.

7.1: Effect on Hydrological Cycle

Aerosol affects hydrological cycle in the forms of Drizzle, Fractional cloud coverage, Cloud thickness and Cloud fraction. Particles warm the layer of the atmosphere where they reside. This warmer air is supposed to hinder formation of the storm clouds. Through suppression of the storm clouds and consequent rain, dust veil is believed to further desert expansion. New observations prove that various clouds may be absorbing more sunlight than expected. Because of the ability of the aerosols in the desert to transport over large distances, the desert aerosols may be the culprit for additional sunlight absorption by some clouds.

7.2: Climatic Effect of Aerosols

Additional reflection caused by pollution aerosols is expected to have an effect on climate comparable in magnitude to rising concentrations of atmospheric gases. Nonetheless, the aerosols' effect will be contrary to the effect of escalating atmospheric trace gases— atmospheric cooling. Knowledge of S-based pollution quantity present in atmosphere is crucial for understanding effectiveness of current SO_2 pollution control strategies.

7.3: Acid Rain

NO_x and SO_2 react with other substances in the air to form acids which fall to the earth like rain, fog, snow and dry particles. Some particles may be transmitted by wind for hundreds of miles. Acid rain damages forests; causes deterioration of buildings, historical monuments, vehicles, and causes lakes and streams to become acidic and thus unsuitable for many varieties of fish.

7.4: Green House Gases

One member of NO_x family, N_2O , is a greenhouse gas. N_2O is accrued in the atmosphere with other greenhouse gases to cause slow but sure rise in earth's temperature. This will lead to a rise in sea level and increased risk or adverse changes to plant and animal habitat.

7.5: Secondary Particles

NO_x reacts with NH_3 , moisture and other compounds to form HNO_3 vapor and related particles like ammonium nitrate (NH_4NO_3), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), ammonium bisulfate (NH_4HSO_4), ammonium bi-nitrate (NH_4HNO_3), ammonium bi-nitrite (NH_4HNO_2) and ammonium bi-sulfite (NH_4HSO_3).

7.6: Water Quality Deterioration

Increased nitrogen load in bodies upsets chemical balance of nutrients used by aquatic plants and animals. Additional nitrogen accelerates "eutrophication," which depletes oxygen and reduces fish and shellfish populations.

7.7: Visibility Impairment

NO₃ particles and NO₂ can block light transmission, reducing visibility in urban areas on a regional scale. The use of reformulated gasoline has resulted in cleaner burning in engines. NO_x and O₃ are transported over great distances. SO₂ and NO_x are transformed in the atmosphere to SO₄⁻ and NO₃⁻, respectively, thus becoming a component of SPM. The detailed composition of these secondary aerosols depends on the local concentration of NH₃, which neutralizes H₂SO₄ and HNO₃ to form NH₄H₂SO₄, (NH₄)₂SO₄ and NH₄NO₃ (<http://www.metolab3.umd.edu>).

8. Air Quality Standards

To develop statements of the relationship between air pollution levels and effects caused by exposure to these levels, many decisions must be made as to the extent of the cause-and-effect relationships. For compliance of national ambient air quality standards, government agencies monitor different pollutants in different places throughout the nation. Sometimes monitoring is conducted by scientists for research purposes (Shandilya, 2002a; Shandilya et al., 2006; 2007). Some issues, which environmental health scientists must deal with to assess these relationships with regard to their usefulness, are:

8.1: Spectrum of Response

Air pollutants can affect health of individuals or communities over a broad range of biological responses. One can easily assume five biological response stages which increase severity of effect: A tissue pollutant burden not associated with other biological changes, Physiological or metabolic changes of uncertain significance, Physiological or metabolic changes that are clear-cut disease sentinels, Morbidity or disease, and Mortality or death. Boundaries among these categories may occasionally overlap. Furthermore, each category shows a range of response rather than a simple all-or-none phenomenon. At any point in time, more harsh effects, such as death or chronic disease, will be obvious in rather small proportions of the population. In few cases death or disease can be credited directly and/or solely to pollutant exposure. Death and disease are end products of repeated cumulative insults (cumulative risks) from sources such as diet, cigarette smoking, physical inactivity, infectious challenges and accidental injury.

Generally, the function of environmental contaminants in the mortality/morbidity experience of a society is not easy to enumerate since many other determinants of death and disease cannot be measured adequately. Larger population portions are affected at these levels. Part physiological responses and physiological changes of uncertain significance are more adaptable to experimental studies on animals and humans than is the case with acute or chronic disease, and they can be more readily associated with specific pollutant exposure. Pollutant burdens are very specific exposure effects which can be quantified in population studies and used as environmental quality indicators. If the link connecting lower and higher response spectrum levels can be recognized, the disease risk linked with pollutant burdens or physiological changes can be exposed. Finally, pollutant exposure role in the whole society's morbidity and mortality experience can be defined.

8.2: Health Disciplines Utilization

Health effect information is helpful for regulatory decision-making from incorporated output of many health disciplines. Major disciplines concerned are epidemiology, clinical research and toxicology. The approach to these disciplines has practical and unique information to offer.

8.2.1: Epidemiology

Epidemiology can give population exposure studies in real-life settings. Advantages of epidemiology are natural exposure, no need for data extrapolation to humans, the most

susceptible groups in the populations can be studied, and both current as well as long-term low-level exposures can be estimated.

8.2.2: Clinical Research

Clinical research studies are sometimes used to collect human data on normal/diseased persons and to conduct in-depth studies of humans accidentally exposed to high-pollutant levels where new study parameters and response indicators can be identified.

8.2.3: Toxicology

Toxicological studies can use various response systems, for instance the whole animal organs, cells, or biochemical systems. The advantages of toxicological studies are maximum dose-response data can be obtained, though this is incomplete at the low end of the curve, data acquisition is rapid; cause-effect relationships are sure, and mechanism of response studies can be performed, such as kinetics of pollutant absorption, distribution, metabolism and excretion etc.

8.3: Pollutants and Human Exposure Response

Effects of pollutant on human health depend on the physical and chemical properties of the pollutant, on the duration, concentration, and route of exposure, and on the human uptake and metabolism of the pollutant. Man's biological response is likewise a function of occupational, psycho-social, and climatological factors and is tempered by phenomena of tolerance and adaptation. These exposure factors motivate attempts to comprehend the impact of pollutants exposure on human health.

8.4: Air Quality Index

Air quality index is defined as a scheme that transforms weighed values of individual air pollution-related parameters into a single number or set of numbers. The result is a set of rules that translates parameter values by means of a numerical manipulation into a more parsimonious form. Ideally, an index or indicator is a mean devised to reduce the large quantity of data down to its simplest form. Of course, during the process of simplification some information is bound to be lost. But if indexing is done in a rational manner, the lost information might not seriously distort the essential meaning of the data (Cohn, 1989). Ott (1978) identified six basic applications of environmental indices namely: A) Recourse applications; B) Ranking of locations; C) Enforcements of standards; D) Trend analysis; E) Public information and awareness; F) Scientific research.

When these index values are compared with a standard rating scale, a clear idea regarding air quality status of a locality is obtained. Thus air quality index system is treated as an efficient step to enhance public awareness against alarming hazards of air pollution.

There are many indices reported in the literature. Air Quality Index (AQI) Recommended by USEPA is an integer value ranging between 0 to 500, indicating roughly air quality status calculated for a particular area with respect to specific pollutants SO₂, CO, O₃ etc. (EPA-454/R-99-010). As the number increases, the degree of pollution also increases. There is a method for reporting AQI which informs the public about air quality status for an area of interest. Shandilya (2002a) has reported ambient air quality status of Delhi city. AQI can have the suitable/applicable "Cautionary Statements" and "Health Effects Statements" along with it.

9. Conclusion

The present article summarizes all aspects of aerosols. It starts by defining aerosols and later classifies aerosols in different manners. Possible natural and anthropogenic sources and transformation processes are outlined. The article describes the physical and chemical characteristics of aerosols. Physical characteristics are detailed in terms of formation process, size, surface, number, volume, mass and shape. Some gases SO₂ and NO_x are described in detail as they affect the atmospheric aerosol load in a significant manner by

undergoing different atmospheric chemical reactions. Impact of aerosols on atmosphere is summarized. The factors affecting chemical reactions are also provided. Regulatory compliances include description of air quality standards, effect of aerosol on human health and different health disciplines closely related. Air quality index for addressing ambient air quality is outlined.

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