CHAPTER I

INTRODUCTION AND REVIEW
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ENVIRONMENT AND ITS DETERIORATION

Intense activities of human beings or the traffic volume, industrial belts, space heating generations (interactions) and domestic populations, they all maintaining such a relation to the modern society which causes great deterioration in the environment. Day by day stability of an environment as a whole is getting a kind of disruption at large in a consequence of deleterious effects on one hand and on the other hand exploitation of the natural resources is also on maximization which has been understood as part of a humankind although power of developing society which accelerates the exploitation of the natural resources may go worse than that if industrialization and urbanization both are not being taken into consideration. Failing in doing so and loss of stability may result as a challenge for the present society to pursuing own activities and which accordingly influences men of the society in their minds, senses or action and also people for get their context, what is right context for pursue and activity. (Oldham, 1973)
Any adverse cause in the prevailing environment living being - material interactions gives much meaning to its own resultant pollution. Such resultant pollution is multidirectional in nature without knowing geographical boundaries and can be said as short term or long term.

The history of air pollution goes back to thirteenth century A.D. During the reign of Edward I (1272 - 1307) there was recorded a protest on the use of "sea coal". In the succeeding reign of Edward II (1307 - 1327) a man was put to torture for filling the air with a pestilential odour through the use of coal. In 1661 a notable pamphlet was published by Royal Command of Charles II consisting an essay entitled "Pumifugium" together with some remedies proposed, writing by John Evelyn.

Records of lethal are far below the levels to cause effects. Under prevailing conditions the only manifestation of air pollution actually noticed by the public at large are visibility and odours (Lodge Jr. et. al., 1981).

Air pollution as defined means the presence in the outdoor atmosphere of one or more contaminants, viz: dust, fumes, gas, mist odour, smoke or vapour in quantities of characteristics and or duration such
as to be injurious to human, plant or animal life or to property, or which unreasonably interfere with the comfortable enjoyment of life and property. The list of air pollutants cover not only the classic items smoke dust, smog, other particulates, \( \text{SO}_2 \) oxides of nitrogen, oxidants and other gases, but also noise heat or cold fog, radioactivity, excess radiation (UV, visible and microwave) and similar substances which satisfy the above definition. Air that becomes less useful through the removal of a normal constituent is also polluted. (Ledbetter, 1972)

**AEROSOL AND DISTRIBUTION:**

Aerosol is defined as a dispersion of solid or liquid particles of microscopic size in gaseous medium with low settling velocities, such as smoke, fog or mist and behave almost like gases. Studies on atmospheric particulate matter have been of interest to scientists for a long time. However, it is only with the industrial development of this century and the air pollution problem associated with the same, the concern about the nature and composition of particulates has simulated research both on their composition and effects. From the viewpoint that health hazard assessment is the ultimate goal, measurement of aerosol is relevant as long as there is sufficient
probability that they will be inhaled by man.

The sources of air pollution are both natural and anthropogenic. The major natural sources include volcanic eruption, meteoric dust, wind risen dust, natural radiation, organic decay, sea sprays pollen, fungi, spores etc. The man made sources include combustion processes, industries, agriculture, construction work, ore smelting, petroleum refining, seavarging processes, transportation etc. (Sitting, 1975).

The combustion processes produce at least five distinct types of particles:

i) The heat vaporises volatile material that subsequently recondense or gets oxidised to non volatile oxides.

ii) The fuel may be converted to SO\textsubscript{2} which is oxidised to sulfate or is condensed as H\textsubscript{2}SO\textsubscript{4} droplets in moist air.

iii) It leaves an ash whose size depends on the initial fuel particle size.

iv) In the absence of oxygen, soot particulates may be formed, predominantly in submicron particles which coagulate to larger particles.
v) Mechanical aspects of fuel handling may entrain coarse ash to uncombusted fuel in large particle range.

The type of pollutants emitted from different sources can be classified as primary under any of the categories: carbon-compounds, nitrogen compounds, sulfur compounds, halogen compounds, fine and coarse particulates and radioactive compounds (Chambers, 1968). The secondary pollutants are more troublesome to abate. These are the products of the interactions between primary pollutants and other atmospheric components. These include, ozone, formaldehyde, organic hydroperoxides, PAN etc. and potentially damaging concentrations of short lived free radicals. The photoactivation is maintained in the presence of sufficient supply of primary and secondary reactants. The process is influenced by many factors like relative concentrations of reactants, degree of photoactivation, variable meteorological dispersive factors, influence of local topography etc. (Chambers; 1968).

An aerosol is a complex system consisting of gas containing suspended particles. Particles are aggregation of matter either solid or liquid larger than individual molecules, the lower size limit for this is in the vicinity of about 0.0001\mu m, but
generally particles approximately above 100 μm are excluded from consideration as suspended particulate matter. The upper limit of particle size is derived from the fact that particles fall out of air rapidly due to higher settling velocities as defined by Stok's law. The approximate settling velocities in still air at 0°C and one atmospheric pressure for particles having density of 1 gm/cm³ observed to have following deposition rates:

<table>
<thead>
<tr>
<th>Size (μm)</th>
<th>Velocity (cm/s)</th>
</tr>
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<tbody>
<tr>
<td>0.1</td>
<td>8 x 10^5</td>
</tr>
<tr>
<td>1</td>
<td>4 x 10³</td>
</tr>
<tr>
<td>10</td>
<td>0.3</td>
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<tr>
<td>100</td>
<td>25.0</td>
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<tr>
<td>1000</td>
<td>390</td>
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Although the mass concentration of aerosols arising from human activities contribute only 7 - 12% of the total aerosol budget, the health and health related effects of even this small fraction are causing serious concern the world over.

The suspended particulate matters can be divided into coarse and fine particulates. Coarse particulates are generally defined as particles having diameter more than 2 μm and upto about 100 μm and generally arise by comminution, whereas fine particulates are smaller than
1 to 2 Um in diameter. Because of their smaller size, fine particulates pose a serious threat to human health. The bulk of the population of particles of sizes below 1 Um arise by condensation from the vapour phase to form very small particles, followed by coagulation (Lodge Jr. et al., 1981).

The total suspended particulate matter (TSP) refers to the entire range of air born particles, whereas fine suspended particulate matter (FSP) is generally thought of as having a diameter smaller than approximately 1 to 2 Um.

Generally, more than 90 percent of the particulates in urban air may be fine (Sproull, 1970), yet despite their numerical importance, this fraction contributes less than coarse particles to a total mass measurement of suspended particulate matter (Lundgren and Paulus, 1975). According to Sproull 1970 and Whitby and Cantrell (1975) coarse particles, which generally represents less than 10 percent of the number of air born particles, may contribute one-half to two thirds of the total mass. A 10 Um particles has a mass 1000 times that of a 1 Um particle, but this coarse mode can constitute as much as 90 percent of the TSP in the atmospheric aerosols particularly in dry windy climates (Lodge Jr. et al., 1981) Particulates
from all these sources are predominantly above 2 \( \text{um} \) in diameter.

Fine particulate matter can be classified as primary or secondary according to their origin. Primary particles are infected directly into the atmosphere. Primary fine particles are mainly emitted by combustion and industrial processes in incineration and refuge burning and transportation systems (Perera and Ahmed 1979). Substances that condense shortly after emission from a high temperature source—because of their low vapour pressure may also be considered primary (Appel et al. 1976) whereas secondary particles are formed from chemical reactions that occur in the atmosphere. Most particles larger than 2 \( \text{um} \) are primary particles. According to a study by EPA in the urban areas 60 to 80 percent of fine particles are formed by secondary reactions involving gaseous precursors. Secondary particles can attain such high numerical concentrations that, despite their small individual mass, they have been shown to make up more than 45 percent of the mass of suspended particulate matter (Staigerwald, 1975).

The presence and availability of particulate
matter in the atmosphere determine whether secondary particles are formed through gas particle reactions (heterogeneous) or by self nucleation of volatile gaseous substances by homogeneous mechanism (Husar and Whitby, 1973). Primary particles are emitted almost exclusively by high energy systems, e.g. combustion, metal processing iron and steel manufacturing etc. (Fennelly 1976). The primary fine particulate material contains a great many different constituents, including soot, flyash metal oxides and salts, sulfates and nitrates.

Another important source of primary fine particulates is motor vehicles. It has been estimated that transportation systems yield only 1 percent globally of the total mass of particulate matter (Fennelly 1976). Studies have indicated that 60 to 90% (by mass) of automobile particulate emission have diameter sizes less than 2 μm (Habibi K. 1973; Mueller et al. 1964; EPA 1973), thus have far greater impact on health and visibility than particulates from many other sources. Other primary fine particulates emitted directly from man made sources and of definite concern for human health are the inorganic mineral fibres and dusts; asbestos, glass fibres, (Perera and Ahmed 1976).
Secondary fine particulates are formed in the atmosphere through homogeneous or heterogeneous chemical reactions and primarily include acid, sulfates, nitrates and organic matter. Precursor substances such as $\text{SO}_2$, $\text{NO}_2$, hydrocarbons, $\text{CO}$, $\text{O}_3$ and $\text{NH}_3$ react in presence of sunlight to form these compounds (Fennelly, 1976; Heicklen, 1976; Hidy, 1975). The hydrocarbon / $\text{SO}_2$ /$\text{NO}_2$ mixture present in the atmosphere is a synergistic mix that promote and accelerate formation of secondary aerosols (Pitts, 1977; Finlayson and Pitts, 1976; Fennelly 1976). In addition, fine particulate carbon iron oxides and other trace elements associated with fine particulate fraction are capable of catalyzing aerosol formation processes. The size distribution of atmospheric particulates is generally found in two modes separated at about 1.5 $\mu$m (.002 to 1.5 and 1.5 to 100 $\mu$m) within which particles share similar chemical composition (Hidy 1975; Dzubay and Stevens 1975; Lundgzen and Paulus, 1975). The smaller size can contain 90 to 99 percent of the number of airborne particles in urban air (Whitby et al. 1972 a; Sproull, 1970) and consists of mostly of man made materials (Fennelly, 1976; Hardy 1976; Hidy 1975) which has greater toxicity than coarse particles (Fennelly, 1976; Labelle et al. 1955).
Whitby and centrell (1975) have demonstrated the atmospheric particulates to have three separate population or modes, with independent existence and behaviour from each other. The first of these is the nuclei (Aitken) mode below 0.1 μm in diameter, and represent in general the recent effluent from combustion sources. These particles are formed by condensation from the gaseous phase and disappear within a short time by coagulation with each other and form slightly large particles. The second one is the accumulation mode between 0.1 to about 2 μm in size, and are virtually permanent features of the atmosphere having a typical airborne life time of few days and are poorly removed by both settling and meteorological processes, coagulate only slowly and thus tend to be very persistent. The third one is of coarse particles above 2 μm in diameter and generally the result of mechanical processes and are readily removed by rain fall and sedimentation reducing their persistence to only few hours in the atmosphere.

The studies of the urban aerosol size pattern exhibit the existence of two separate generalised size ranges. The total or regional aerosol composition show a general bimodality of particle size distribution that is reflective of their origine.
A fine particulates generally result from human activities, the ratio of fine to coarse particle mass concentration varies widely in both urban and non urban sites. Whitby and Cantrell (1975) have observed mass concentration ratios of 0.02 and 3.2 of fine to coarse particulates in the marine (California Coast) and very polluted (St. Louis) areas respectively. The difference in percentage of TSP mass in these sites varied greatly from 2 to 76 per cent.

Bimodality is also observed in the distribution of chemical constituents. Most of the air born sulfates, nitrates and organic compounds as well as primary emission materials from combustion and metal refining sources are present in the submicron range.

AIR POLLUTION AND EFFECTS (GENERAL):

Impairment of visibility if perhaps the most noticeable and best documented effect of particulate matter (Robinson 1968). Regional haze is relatively homogeneous and can occur on a geographical scale ranging from an urban area to remote regions. The photochemical smog which reduces visibility has become a regular phenomenon in industrialized cities. Nearby objects can appear flattered and discoloured and scattered light is perceived as a
grey or brown base. Visual range measurements at airports are a usual indicator of the extent of intensity of regional haze.

Since the passing of clean air act in the developed countries and its amendment, both atmospheric scientists and government regulatory agencies have shown growing interest in quantitatively characterizing visibility and the extent to which visibility is threatened by pollution. The various non-health effects of air born particulate matter have been excellently reviewed by Lodge Jr. et. al. (1981) It is thought that visibility is not only an aesthetic blight, but is an indicator of particulate pollution linked to acid precipitation and health effects (Sloane, 1982).

The health associated risks of exposure to high levels of particulate matter include

1. effects on respiratory mechanisms and symptoms
2. aggravation of existing respiratory and cardio vascular diseases.
3. effects on clearance and other defence mechanism.
4. Morphological alterations
5. Carcino-genesis and
6. Mortality
The results of a number of cross sectional studies on mortality and air pollution reviewed recently (Lipfert, 1985) Evans et al; 1984) indicate good correlation between excess deaths with TSP and acidic fumes. The population that appear likely to be most sensitive include (a) individuals with chronic obstructive pulmonary or cardiovascular diseases (b) asthmatics (c) the elderly, (d) children (e) smokers (f) mouth or oronasal breathers.

An evaluation of the mechanism by which inhaled particles ultimately may affect human health must recognize the deposition and clearance in the respiratory tract, more specifically in the extrathoracic, tracheal-bronchial or alveolar region.

Upon deposition particles may produce physiological and ultimately pathological effects by a variety of mechanisms although the respiratory tract is equipped to remove inhaled foreign materials, but when particles exposures are sufficiently high or if clearance mechanisms are impaired accumulation of particles may reach levels that produce responses. The major mechanisms by which particles potentially produce effects can be categorized as follows:

(a) Chemical and mechanical irritation of tissues or nerve receptors at the site of deposition.
(b) Alteration of host defence systems particularly clearance mechanisms leading to susceptibility to infection and potential development of chronic lung diseases.

(c) Direct or indirect damage leading to morphological changes.

(d) Systematic toxicity, particularly of toxic particles and polycyclic organics to other parts of the body.

**AEROSOL AND CHEMISTRY**

This is to investigate the role of pre-existing aerosol in the conversion of $\text{NO}_2 \rightarrow \text{NO}_3$ and in the complex - reactions occurring during a smog episode. Such an episode is characterized by the combined reactions of NOx and hydrocarbons under the influence of solar irradiation, leading to ozone and a variety of toxic gases. The preexisting aerosol in a smog situation could have the following influence.

(1) Aerosol surface in the atmosphere might catalyzed the formation of certain compounds and this superstition is supported by the fact that some of the reactions occurring in smog chambers are heterogeneous in nature, if the formation of the photocatalitically highly reactive HNO$_2$ (nitrous acid), as well as the formation of HNO$_3$ acid.
(2) Reactive intermediates might be scavenged by aerosols thus leading to a decreased formation of specific products.

(3) Low volatile products might condense on pre-existing aerosol in the ambience which might not occur in the absence of aerosol in simulations in smog chambers due to well scavenging of this considerable material. Therefore the presence of primary aerosol in smog chambers would be a better simulation of ambient smog conditions.

Aerosols are formed by commution by condensation from supersaturated vapors and by gaseous chemical reactions. It has been accepted that, particles less than 1 um diameter arise from condensation and larger one from commution. Diameter of air born particles in general range from $6 \times 10^{-4}$ um. to about $10^3$ um. Particles larger than 10 um are rapidly settle out of the air by gravity and particles less than 1 um eliminated by process of coagulation into larger entities, leaving the vast majority of air suspended particles that remains in a natural aerosols in the range of (0.1 to 10 um). Most of the earlier studies are concerned with the particle size distribution of aerosols in the range of 0.1 to 10 um recent years, which in general report that the mass distribution of atmospheric...
aerosols is usually biomodal with one mode occurring below 1 um and another in the 5-15 um range. Total aerosols is composed of two different population natural and anthropogenic model diameter of 0.4 to 0.6 um and 3-5 um respectively and follows log normal distribution. On inhalation particle larger than 10 um are essentially removed in the nasal chamber and down to 2 um are deposited 100% in the pulmonary air spaces. Below this size removal efficiency falls off to minimum at about 0.5 um. Miller et al (1975) has defined the air born particles of 15 um size as inhalable and of present is the EPA recommended standard for inhalable particles. Till recently, a meager information on particle size distribution of SPM is available for India. Very high SPM level are reported for Indian urban centres as compared to western counter part. In this condition, the particles size distribution study of SPM become most important task so as to find out the hazardous nature of it.

The Aerosol Collection, for many reasons aerosols are supposed to important

(1) To determine whether there are hazardous concentration of pollutants in the atmosphere or if ambient air standards have been exceeded.
(2) To determine the effectiveness of control programmes in reducing ambient concentration of pollutants.

(3) To determine the emission levels from a source.

(4) To determine the effectiveness of control equipment.

(5) To determine the sources contributing to pollution at a receptor.

(6) To identify pollutants in the atmosphere.

In recent years concern has been universally voiced regarding environmental pollution arising as a side effect of industrial activities. In national situation with the growth of industries, more and more toxic substances are either used as raw materials or given off during manufacturing processes in the form of dusts, fumes, vapors and gases. These pollutants ultimately dissipate in working environment and pose occupational health hazard. According to a U.S. estimate there are some half a million man made substances already present as pollutants in our total environment. Every year some (400-500) new chemicals are said to be added, many of these chemicals are toxic to human being and may produce chronic effect, on the human organ like lungs, kidneys and heart. Besides even cancer
results from some types of occupational exposure. Apart from this, these pollutants get into the air and water and thus disturb the ecological balance of nature. Environmental monitoring is the application for all kinds of air monitoring of the working places is essential for installing the appropriate control measures or to confirm the adequacy of engineering control measures. It further helps in diagnosing early cases of poisoning and limiting absorption of toxic chemicals before biochemical or enzyme mechanisms are interfered with significantly. It also helps in the proper selection and placement of workers in the working environment. To start with the environmental monitoring, first a preliminary survey of working place is desirable to get acquainted with the processes, frequency of operations, raw materials and final products. The role of surfaces as a catalytic agent for formation of reduced nitrogen species is not considered. Primarily it is wished to determine if liquid phase chemistry is capable of accounting the $\text{NO}_3^-$ levels of the order to those levels of the order to those observed in the south coast Air Basin. The analysis is appreciable to the general atmosphere in ascertaining the possible explanation for the observed differences in $\text{NO}_3^-$ and $\text{SO}_4^-$ size distribution.
HETEROGENEOUS FORMATION OF NITRATES WITH GAS

PHASE CONVERSION (NO\textsubscript{2}/SO\textsubscript{2})

SO\textsubscript{2} may be converted to SO\textsubscript{4} by homogeneous or heterogeneous path. In clean air, SO\textsubscript{2} is very slowly oxidized by sun light to form sulfuric acid, at a rate of about 0.1%. In the ambient atmosphere, SO\textsubscript{2} oxidation may occur at rates exceeding 10%/h. In the gas phase, reactions with free radicals provide the major contribution to homogeneous oxidation of SO\textsubscript{2}. In the liquid phase catalytic oxidation of SO\textsubscript{2} takes place in the presence of metallic compounds such as Mn, Fe, Vn, Al, Pb and Cu. In aqueous droplets an acid pH decreases the rate of SO\textsubscript{2} oxidation and therefore H\textsubscript{2}SO\textsubscript{4} formation in the aerosol is self limiting unless the activity is diluted by additional water vapour or buffered by alkali metal compounds or ammonia because of the high acidity of droplets containing dissolved oxides of nitrogen in addition to SO\textsubscript{2} and NH\textsubscript{3}, virtually no sulfate will form in the droplet through oxidation of sulfite ion in the absence of metallic catalysts. A quantity of interest in the evaluation of atmospheric particulate sulfate and nitrate concentration is the ratio of the actual concentration of ammonium ion to the stoichiometric concentration of ammonia needed if all the SO\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3}\textsuperscript{-} concentrated existed as their
ammonia salts i.e. \[
\frac{[\text{NH}_4^+]}{[\text{NO}_3^-] + 2 [\text{SO}_4^{2-}]} \]

in the gas phase then the condensation coefficient is \(1.24 \times 10^{-6} \text{cm}^3/\text{min}\) regardless of the \(\text{NH}_3\) concentration.

In either case it is clear that \(\text{NH}_4\ \text{NO}_3\) precipitation must be an important processes in the atmosphere

\[
\text{HNO}_3 + \text{Cn} \leftrightarrow \text{CnHNO}_3
\]

\[
\text{NH}_3 + \text{CnHN}_2\text{NO}_3 \rightarrow \text{Cn} + 1
\]

when \(\text{Cn}\) represents particulate \(\text{NH}_4\ \text{NO}_3\) with \(n\ \text{NH}_4\ \text{NO}_3\) molecules. The life time might be larger either because for particles other than \(\text{NH}_4\ \text{NO}_3\), absorption of \(\text{HNO}_3\) may not occur with unit efficiency or because of the 1000 folds lower concentrations of \(\text{NH}_3\) in the atmosphere reaction. If \(\text{NH}_4\ \text{NO}_3\) is associated in the gas phase, then the condensation coefficient is \(1.24 \times 10^{-6} \text{cm}^3/\text{min}\) regardless of the \(\text{NH}_3\) concentration.

In either case it is clear that \(\text{NH}_4\ \text{NO}_3\). Many of the pollutants in urban atmosphere even at extremely low concentrations both with each other and with the normal constituents of the atmosphere although some of these reactions remove or scavenge pollutants and thus act to cleanse the atmosphere. Other atmospheric chemical reactions, however produce products that are much detrimental to the poor visibility. It is one of the most obvious manifestal of photochemical smog. Visibility is reduced because of small particles (0.1 to 1 um in diameter) suspended in the atmosphere which scatter light
very effectively.

**FOG FORMATION:**

When the atmosphere becomes supersaturated in water vapour, usually because of a temperature drop, condensation of H₂O occurs producing a fog. A fog typically contains particles of 7 to 15 nm diameter with a no density of 50 to 100/cm³ for a light fog and 500 to 600/Cm³ for a heavy fog (10^{15} to 10^{17} liquid) H₂O molecules /Cm³ of air (Amelin 1966). Since even clean air contains 10³ particles/Cm³ of air (Amelin 1966) and urban air often contains 10⁴ to 10⁵ particles/Cm³. These are sufficient particles so that condensation will be heterogeneous and occur on the particles. The equilibrium vapour pressure of H₂O depends on the drop size but it is only 1% higher for droplets of 0.1 nm diameter than for infinitely large particles. Since the mean diameter of particles in urban air are 0.4 to 0.8 nm the supersaturation will be negligible before condensation occurs. In fact if the condensation nuclei are soluble in water then condensation occurs below the vapour pressure of H₂O because the soluble species reduce the vapour pressure. If Raoults law is obeyed (ideal solution) then for example
condensation nuclei can grow to 90 mole% H₂O at only 90% relative humidity. However if the temperature drop is sufficiently sharp the heterogeneous nucleation is not fast. The supersaturation raises and homogeneous nucleation occurs. This gives rise to $10^5$ water droplets/cm³ but they will be relatively small if 2.5 Torr of H₂O vapour condenses into $10^5$ particle/cm³, the the mass average particle diameter is 3 ℓm most of which is $<1$ ℓm diameter.

The rate of water vapour removal can be computed from condensation coefficients. They are diffusion controlled and increase proportionally with the diameter of the particle reaching $2 \times 10^{-5}$ cm³/Sec for a particle of 1 ℓm diameter. For a H₂O vapour pressure of 30 Torr (10¹⁸ molecules/cm³) vapour pressure at 29°C, the life time required for a particle to grow to a droplet containing $3 \times 10^{13}$ H₂O molecules (10 ℓm diameter) would be 50 Sec for 1% supersaturation. At lower H₂O vapour pressures and lower supersaturations, the times involved could reach on hour or more. In photochemical smog the end product of NO oxidation is HNO₃. The HNO₃ can react with NH₃ or other materials to give nitrate. The formation of pNO₃, ammonium nitrate has been studied extensively but not in
Indian condition. Mixtures of oxone and ammonia were reacted in N₂ or air to produce HNO₃ in situ. The HNO₃ could then react with NH₃ in the vapour phase.

\[
\text{NH}_3^- (g) + \text{HNO}_3 (g) \rightleftharpoons \text{NH}_4\text{NO}_3 (g).
\]

It is not yet known what fraction of the HNO₃ is free and what fraction becomes tied up as a gaseous NH₄NO₃. Evidence suggests that equilibrium is shifted entirely to the left but more recently with the accumulation of more experimental data the evidence favours the equilibrium being shifted to the right under the experimental condition. The position of the equilibrium is rather important because it determines the condition under which NH₄NO₃ precipitates. If the original interpretation is valued then homogeneous nucleation of NH₄NO₃ commences with the product \([\text{NH}_3][\text{HNO}_3] = 5.8 \times 10^{27} \text{molecules}^2/\text{cm}^6\text{at 25°C}
\]
This would correspond to conditions when if \([\text{NH}_3]= [\text{HNO}_3]\) then concentration would be 3 ppm much higher than would even be realized in the atmosphere. However this value is the particle nucleation pressure and not the vapour pressure, which is unknown and must be at least an order of magnitude lower, since NH₄NO₃ is quite nonvolatile. The nucleation reaction corresponding to this situation was found to be

\[
q \text{ HN} + q \text{ HNO}_3 \rightarrow (\text{NH}_4\text{NO}_3) \quad \text{with the}
\]
\[
q = 8 \quad \text{and} \quad k_c = 6.2 \times 10^{24} \text{cm}^{45}/\text{min}.
\]
European pollution constant on the other hand with the later interpretation the equilibrium in reaction (2) is shifted to the right and the critical $\text{NH}_4\text{NO}_3(g)$ pressure needed to initiate nucleation at $25^\circ\text{C}$ was $1 \times 10^{12}$ molecules/\text{cm}^3 (40ppb) both in the presence and absence of H$_2$O, so that HNO$_3$ would never accumulate in the vapour phase (in the presence of NH$_3$). In this case the nucleation reaction is

$$q = \frac{\text{NH}_4\text{NO}_3(g)}{(\text{NH}_4, \text{NO}_3) g}$$

$$q = 9 \text{ and } K(4) = 3 \times 10^{-108}\text{ cm}^{-24}\text{ /min}$$

Regardless of which mechanism applies, once particulate NH$_4$NO$_3$ can condense is present, removal of gaseous HNO$_3$ or NH$_4$NO$_3$, as the case may be proceed rapidly by condensation, if free HNO$_3$ is present.

The concentration of air pollutants in the ambient air and hence their impacts are determined not only by the rates of emissions and chemical transformations but to a very large extent by meteorology for e.g. As you might have seen episodes of London meteorological conditions were such that the pollutants were effectively contained in relatively small volumes leading to high pollutant concentrations. In the lowest 10 km, of the earth atmosphere in the air temperature generally decreases with altitude at a rate of 7$^\circ\text{C}$ per kilometer;
this is known as positive lapse rate. In this normal troposphere warm air close to the earth surface being less dense rises and replaced by cooler air from higher elevations. This results in mixing within the troposphere.

In some situations, however the temperature of the air at some height within the troposphere may start to rise with increasing altitude before reversing itself again that is the lapse rate changing from positive to negative to positive see figure 1. This region with the negative lapse rate is known as inversion layer, in effect, it acts as a lid on an air mass the cooler air underneath it, being more dense will not rise through it. In effect pollutant trapped below the inversion layer are not mixed throughout the entire troposphere but are confined to the much smaller volume beneath the inversion layer, this results in much higher ground level concentrations. The formation of thermal inversions is of the most important meteorological factor contributing to air pollution problem in urban areas. The two classic types of air pollution, London or sulfurous and Los Angeles or photochemically generally have different types of thermal inversion associated with item. See figure 1.
Variation of temp. with altitude within the troposphere

(a) Normal lapse rate

(b) Change in lapse rate from positive to negative a characteristic of thermal inversion.

Interestingly the vertical distribution of photochemical oxidant may not be such that it fails of rapidly at the inversion layer. In fact in a classic series of experiments, Edinger and Co-workers (1972-1973) showed that oxidant concentrations in the Los Angeles air basin could be higher within the inversion layer than at ground level. Figure 2.
Several layers of oxidant exist within the inversion layer, reaching concentrations as high as 0.2 ppm compared to a ground level concentration of 0.1 ppm. When the inversion layer is deep and strong much of this rising polluted air does not get sufficiently warm to penetrate the inversion completely, so it moves out and away from the slopes and remains within the inversion layer - multiple pollutants peaks within the inversion layer result.

Figure 2.

temperature and oxidant profile (June)
The role of meteorological transport in establishing the concentrations of various sources to downwind ambient pollutant concentrates is clearly important not only for pollutants within a given air basin but also for longer-range transport situations. An important current problem is to find appropriate tracers for long-range transport (1000 km or more) studies of acid deposition. Such tracers must not have other natural or anthropogenic sources, must not react in the troposphere and must be non-toxic. Long-range transport also plays a role in ambient O3 concentrations for e.g. Eliassen and Coworkers (1982) have shown that some of the O3 observed in Scandinavia must come from other European countries including the USSR and Poland.

CHEMICAL TRANSFORMATION

Brief consideration of emission, meteorology overview of atmospheric chemical transformation is important. It summarizes major features of air pollution chemistry. It will serve as useful background material because it is set off on detailed discussion of the fundamental and applied aspects of tropospheric chemistry. The primary pollutant NOx (mainly NO2) reacts in the presence of light Fishman and Colleagues calculated that doubling the tropospheric ozone content may increase the surface temperature by nearly 1°C, which is substantial compared to the 2-3°C temperature increase calculated for a
doubling of CO\textsubscript{2}.

**SPECULATION ON PARTICULATE:**

Particulate species occur in the form of nitrate and sulfate. The relative contribution of particulate and gaseous deposition to total dry deposition is not certain but given the low velocity of particulate deposition, gaseous deposition is considered to be more important. The velocity of deposition depends upon particle size for particle diameter 0.02 microns - 0.025 cm/sec for diameter 0.2 microns - 0.6 cm/second and for diameter 2 microns - 0.1 cm/second. Also, as far as vegetation is concerned, gaseous deposition is far more important as absorption of gases is much faster than intake of particles. The rate and extent of gaseous deposition vary according to the chemical species, meteorological condition and the receiving medium. Estimates for SO\textsubscript{2} deposition range from 0.1 cm/sec to 2 cm/second, for NO\textsubscript{x} there are far fewer measurements and estimates range from 0.01 cm/second to 0.8 cm/second. NO\textsubscript{x} is oxidised faster to nitrate than SO\textsubscript{2} is to sulfate over long distances SO\textsubscript{2} increasingly predominates as the major dry acid pollutant deposited.
DEPOSITION:

Far the most part sulfuric acid and nitric acid dissolve in a water medium and are brought to the ground by precipitation. The dissolved acids consist on sulfate ions \( \text{SO}_4^{2-} \), nitrate ions \( \text{NO}_3^- \) and hydrogen ions \( H^+ \) though some tends to be neutralised by ammonia where upon ammonium ions \( \text{NH}_4^+ \) are formed.

Wet deposition is characterised by the following two processes.

(a) rainout - where by atmospheric species are associated with cloud phenomena;

(b) Washout - where the species are removed by falling precipitation.

The process of rainout is not yet well understood, whereas there is more general understanding concerning the washout process.

Countur map - It is good for background or zero ground of \( \text{P.NO}_3 \), where is source to find the level of concentration (Delhi map - helps much what is countur).

Rainout - It is generally accepted that as emissions disperse sulfurdioxide and nitromendioxide gases convert to sulfate and nitrate aerosols and at long long distances the aerosol phase is dominant rather
than the gaseous phase. It is not known whether $\text{SO}_2$ gas absorbed into cloud water and then oxidised to sulfate before being removed in rain or whether the major process is nucleation of cloud droplets on sulfate particles, already produced from sulfur dioxide during transport in dry weather condition. Many studies indicate that aerosols tend to be more readily scavenged by rainout processes such as condensation than by the washout process such as capture by falling droplets. Thus sulfate and nitrate aerosols are thought by some to act as cloud condensation nuclei. In addition particulate material containing sulfate and nitrate are captured by cloud droplets via impaction, interception and Brownian diffusion.

In the washout process, pollutants are removed from the atmosphere by falling precipitation but below cloud level therefore processes which characterize rainout also occur in the washout process for example the washout of particulate material is seen to be achieved by impaction, interception by falling rain drops and Brownian diffusion effects, though the latter process is considered to be of little importance to the washout of sulfate and nitrate aerosols. It seems that the washout of $\text{SO}_2$ by rain falling through a concentration of $\text{SO}_2$ is
Oxidation

\[ \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 \]

Conversion

\[ \text{H}_2\text{SO}_4 \rightarrow 2\text{H}^+ + \text{SO}_4^{2-} \]

\[ \text{HNO}_3 \rightarrow \text{H}^+ + \text{NO}_3^- \]

\[ \text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+ \]

Dry deposition

Runoff

Leaching

Transport

Effects on vegetation

Effect on water chemistry and water biology

Humus layer

Mineral soil

Environment and acidification

Swedish Ministry of Agriculture Environment '82 Committee.

Diagram No. 1
influenced by the size of rain droplets, the pH of rain and of course the extent of SO₂ concentrations. For example large raindrops are less effective at capturing and dissolving atmosphere SO₂ than small rain droplets. Heavy rain, characterised by large deolets will therefore tend to have lower SOx concentrations than light rain falling through the same atmosphere.

The presence of ammonia is said to be enhance the rate of removal of SO₂ as ammonia helps to neutralise the rain medium. In the case of NOₓ very little work has been carried out on the final washout of these species.

ENVIRONMENT AND ACIDIFICATION: See diagram no. 1

The nitrogen in the oxides of nitrogen (NOₓ) derives from two sources, there is the nitrogen that is present in the soil or minerals and the atmosphere, of which this gas constitutes eighty per cent. To all intents and purposes therefore the amounts of NOₓ that could be formed are unlimited in the environment. The amounts that are formed will depend on how combustion is carried out and at what temperature. The higher the combustion temperature
the more $\text{NO}_x$ obtain. In the densely populated industrialized area larger quantities of $\text{NO}_x$ are released from domestic industrial and automotive exhausts. After discharge into the environment it goes through many chemical and photochemical reactions resulting to the acidification of the environment due to the activity of nitrates and sulfate aerosol. Assessment of various reactions in the troposphere. Elementary reactions are defined as those that can not be broken down into two or more simpler reactions. Generally it consist of one or two reactant species and are referred to as a unimolecular and bimolecular processes respectively. However there are a number of important gas phase processes in which three different species participate these are termed as molecular reactions. In the troposphere it usually involve $\text{N}_2$ and or $\text{O}_2$ as one of the three participants, the role of third molecule is generally to act as an inert gas which stabilizes the energy rich product from highly exothermic bimolecular reaction by siphoning off the excess energy and thus preventing the dissociation back into the reactants. In such cases, rather than being specific as to the colliding third body the symbol $M$ is used, examples are given below thermal decomposition of $\text{PAN}$ unimolecular
The formation of ozone by the reaction of ground state oxygen atom.

\[ O_3 + \text{No}_2 \rightarrow \text{NO}_3 + \text{O}_2 \] (1)

Because \( M \) does not enter the reaction chemically such reactions are written with the 'M' above the arrow \( O (3p) + \text{O}_2 \text{ M} \rightarrow \text{O}_3 \). It seems that in majority of the reactions it is dealt with in the atmosphere are bimolecular, with a lesser number being termolecular.

An example of an overall reactions is the oxidation in air of methane by \( \text{OH} \) radicals in the presence of \( \text{NO} \). The major stable products formaldehyde (\( \text{HCHO} \)) and \( \text{NO}_2 \) are formed in a sequence of five elementary reactions (chain reactions)

\[ \text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O} \] (4)

\[ \text{CH}_3 + \text{O}_2 \text{ M} \rightarrow \text{CH}_3\text{O}_2 \] (5)

\[ \text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \] (6)

\[ \text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2 \] (7)

\[ \text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH} \] (8)
Chain reaction with the initiating step being reaction (4) and the chain carrying steps which regenerate OH radical being reaction (5) - (8). OH can react with NO₂ to give nitric acid and NO₂ can self recombine to form hydrogen peroxide and O₂

\[ \text{OH} + \text{NO}_2 \xrightarrow{M} \text{HNO}_2 \]
\[ 2 \text{HO}_2 \xrightarrow{M} \text{H}_2\text{O}_2 + \text{O}_2 \]

These are elementary chain termination processes because the OH and HO₂ radicals from molecular products that are relatively stable in the troposphere that is HONO₂ and H₂O₂.

**AIR POLLUTION SYSTEM:**

Since the foundations of tropospheric chemistry were established to a large extent by air pollution researches. It is useful in aspects of the subject within the conceptual framework of an air pollution system fig. 2. Another phenomenon that affects NOX is the photochemical reactions (with or without ozone). This development of correlation ship could be a total indicative of photochemical pollution, that is the main contribution to nitrogenous SPM and particularly to that fraction which makes respirable particles. The implications
of this conclusions are very important for emission control strategy and protection of public health in NOx emission. Considering these above facts it is very essential to understand mechanism of nitrate from NOx and to bind out the possible influences of other factors like water vapour and aerosoles on the transformation velocity of NO2 to HNO3 acid. SPM present out in the atmosphere is highly significant for its size. The diameter range varying from 0.02 to 500 µm diameter, resembles that of a gas and is identical to gas diffusion. Such small particulates easily absorb gases, collide with each other and undergo adhesion. Hence it seems to be important with respect to size distribution under certain environmental variables and is of concern for human health. SO2 and NOx are emitted from industrial complexes and towns some of these gaseous oxides stick to the ground showing dry deposition. This may happen near the emission source or at a great distance from it. The longer the SO2 and NOx remain in the air, the greater is the likelihood that they will undergo oxidation thereby forming sulfuric acid (H2SO4) and nitric acid (HNO3). For the most part these acids dissolve in cloud droplets and raindrops and are brought to the
ground along with the precipitation. Some of the acid is neutralised by such substances as ammonia, where upon NH₄⁺ ions are formed. The dissolved acids consist of sulfate ions, nitrate ions and hydrogen ions (H⁺) when these various ions rain down it is called wet deposition. The effects of acidification are the results of indirect action by the sulfur and nitrogen emissions. An influence that it exerts on living organisms through the changes it bring about in water and soil. These effects are in relation to the size of the deposition (both the dry and the wet) and to the inherent sensitivity of the soils and the waters. Thus the acidification only becomes apparent when the combination of these factors is at its most unfavourable. The effects may therefore be felt both in the immediate vicinity of an emission source and upto great distances away from it. The most important among the direct effects of SO₂ and NOx in the air are the harm done to human health, damage to plants and atmospheric corrosion. The direct effects are determined by the concentration of the pollution in the air. See diagram 2.
CONCEPTUAL FRAME OF AN AIR POLLUTION SYSTEM

- Sources - Motor Vehicles, Industry, Power Plants, Domestic Natural
- Control Measures
- Legislation
- Emissions of Primary Gaseous Pollutants (SO₂, NOₓ, NMOC, NH₃, CO, Particulate...)
- Chemical and Physical Transformation to Secondary Pollutants H₂SO₄ and SO₄, HNO₃ and NO₃, Photochemical Oxidants O₃, PAN, H₂O₂, Free Radicals, HCHO, HNO₂, and Organic Part.
- Meteorology Dispersion and Transportation Plan, Plumes, Clouds, Fog, Rains, etc.
- Control Strategy Options
- Monitoring
- Ambient Air
- Plume Airshed and Long-range Transport Mode
- Wet and Dry Deposition, Acid Rain, etc.
- Photochemical Air Pollution e.g. O₃
- Impact on Receptors, Humans, Animals, Plants, Lakes, Materials, Visibility

DIAGRAM NO. 2
TRANSPORT AND TRANSFORMATION OF NITRATE IN ENVIRONMENTAL AND BIOLOGICAL MEDIA

The continuous interchange between atmosphere and terrestrial \( N\text{-No}_3 \) takes place along a number of different pathways including air, water, soil, microorganisms, plants, animals and man. \( N\text{-No}_3 \) has undergone profound modifications through the agricultural and industrial activities of man (Bolin & Arrhenius, 1977; Committee on Nitrate Accumulation, 1972; Commner, 1970; FAO/IAEA Panel of Experts, 1974).

Nitrogen of atmosphere is in the form of dinitrogen molecule \( (N_2) \) the great strength of the double bond is mainly responsible for its chemical inertness. A part of nitrogen is transformed by microbial action and incorporated into living organisms and called fixation and is estimated to amount globally to 150 million tonnes of fixed nitrogen per year. In industrial nitrogen fixation, nitrogen of atmosphere is combined with hydrogen at high temperatures and pressures in the presence of suitable metal catalysts (Haber - Bosch) to produce ammonia. Industrial nitrogen fixation accounts for one
quarter of the total world production of fixed nitrogen (Bolin & Arrhenius, 1977) Reduction to ammonia \((\text{NH}_3)\) can be accomplished by only a limited number of organisms. Symbiotic nitrogen fixation takes place in the root nodules of legumes such as soya bean, clover and alfalfa which contain bacteria like rhizobium species. There are also symbiotic processes with plants other than legumes involving, for e.g. some cyanobacteria. A number of free bacteria and algae can also fix nitrogen (Burns & Hardy, 1975; Quispel, 1974). The fixation is catalyzed by a complex enzyme nitrogenase(1,7.99.2) Ammonia produced by biological fixation is then converted to nitrite and nitrate by the process of nitrification. Plants can assimilate only a part of the nitrates present in soil, some leaches into ground water and rivers and may reach estuaries and oceans, the rest is subjected to denitrification. Denitrification takes place in the soil and also at the interface between water and sediment in oceans, rivers, lagoons and lakes, \(\text{N-NO}_3\) from natural fixation and artificial fertilizers are ultimately used for the synthesis of biological molecules, particularly proteins. According to Delwiche (1970) nitrogen fixation on a world basis may exceed denitrification by about 10%. The
TRANSPORT AND TRANSFORMATION OF NITRATE IN ENVIRONMENTAL AND BIOLOGICAL MEDIA

DIAGRAM NO. 3
increased use of industrial fertilizers has resulted in some areas in increased concentration of nitrates in bodies of water, resulting in some cases, in eutrophication. See Diagram number 3.

REACTION OF NO₃⁻, NO₂⁻ IN ITS OWN ENVIRONMENT:

In the environment both NO₂⁻ and NO₃⁻ ions can be formed from the ammonium ion (NH₄⁺) in a two step oxidation.

\[
2 \text{NH}_4^+ + 2\text{OH}^- + 3\text{O}_2 \rightleftharpoons 2\text{NO}_2^- + 2\text{H}^+ + 4\text{H}_2\text{O} \quad (1)
\]

\[
2 \text{NO}_2^- + \text{O}_2 \rightleftharpoons 2\text{NO}_3^- \quad (2)
\]

These reactions are mediated by different microorganisms.

1. Reaction of an aerobic chemolithotroph
   Nitrosomonas, reaction.

2. By Nitrobacter which obtains almost all its energy from the oxidation of NO₂⁻.
SOURCES OF NITRATES (NO₃⁻) AND NITRITES (NO₂⁻) IN AIR:

Artificial fertilizers, a major source of environmental nitrates, may be composed of a variety of chemicals, including ammonium, calcium, potassium, and nitrates of sodium and urea. The production of nitrogenous fertilizers in the world has increased in terms of nitrogen (N) from 15.8 million tonnes in 1961/62-1965/66 to 42.3 million tonnes in 1974/75. (United Nations, 1976)

The fact that plants can not use soil nitrogen completely is of great significance nitrogen utilization may vary from 25 to 85% depending on the crop and on agricultural techniques. Thus to obtain maximum production, a great excess of nitrogen fertilizer must be applied to the soil and the resulting nitrogen run off will be substantially increased. For eg. Kohl et al. (1971) showed that as much as 55 - 60% of the nitrogen input in the Sangamon River feeding Lake Decatur, IL, USA, was of fertilizer origin Lee (1970b), Sawyer (1947) and Sylvester (1961), have all published data showing that nitrogen run off is 3 - 10 times higher from fertilized areas than from unfertilized areas in the same region. However, analysis of stream waters did not show a clear relationship between the NO₃⁻ concentrations in
British rivers and the amounts of fertilizers used on adjacent land (Tamlinson, 1970)

ANIMAL SOURCES:

Another major source of nitrates is farm animal wastes which contain large amounts of nitrogenous materials that may be converted into nitrates ($\text{NO}_3$). The problem is more acute where farming is carried out intensively, a common practice in North America for both livestock and poultry. Since a 450 kg. steer excreta about 43 kg. of nitrogen per year, a 3200 head feed lot would produce 1400 tonnes annually on a relatively small area - an amount equivalent to about 260000 people. Thus such feed lots become "small area" sources of nitrogen run off only 10% of these wastes is returned to cultivated land (Standford et al, 1969) and run off studies demonstrate a considerable problem of environmental pollution. Mye (1973) reported Gilbertson et al (1970), who found that the total nitrogen concentration in runoffs ranged from about 50 to over 5500 mg/litre. Animal husbandry, even when carried out on pastures or with the return of the animal wastes from maximum of 7-8 cows could efficiently be used per hectare of farm land or pasture and that higher
application rates might raise $\text{NO}_3$ levels about 10 mg/litre in the subsoil waters.

**NITRATES AND EFFECTS ON MAN**

In the erythrocytes of healthy individuals, the process of methaemoglobin formation and reduction is continuous. The mean content of methaemoglobin in healthy populations is usually reported to be below 2% of the total haemoglobin concentration (Committee on $\text{NO}_3$ Accumulation, 1972; Gobbi et al, 1974; Smith, 1972). However, Goldsmith et al (1975) recently found mean levels in Californian populations ranging up to 2.11% with 1% of the adults and 8% of infants having methaemoglobin levels exceeding 4%. Higher values are found in premature than in full term infants and levels in infants are higher than those in older children and adults (Kravitz et al, 1956). At a level of about 10% methaemoglobinemia may produce symptomless cyanosis accompanied by hypoxic signs and symptoms, such as weakness, exertional dyspnoea, headaches, tachycardia and loss of consciousness (Arena, 1970; Committee of Nitrate Accumulation, 1972; Jaffe & Heller, 1964). The lethal concentration of methaemoglobin is not known, but death may occur at
levels exceeding 50% (Committee of Nitrate Accumulation, 1972).

TOXIC BEHAVIOUR OF NITRATES:

Acute nitrate poisoning was first recognized in cattle by Mayo as early as 1895 (Wright & Davidson, 1964), while Comly (1945) was the first to report nitrate (\( \text{NO}_3^- \)) poisoning from well water in infants in the USA. As a result of these and other reports, several studies have been conducted on the toxicity of nitrates (\( \text{NO}_3^- \)). They are mainly centred on the formation of methaemoglobin that accompanies excessive exposure to \( \text{NO}_3^- \) and \( \text{NO}_2^- \). The acute toxicity was recently reviewed by the committee on \( \text{NO}_3^- \) accumulation. Although the outstanding feature of \( \text{NO}_3^- \) toxicity is the development of methaemoglobinemia, \( \text{NO}_3^- \) may also cause vasodilation which aggravates the effects of the methaemoglobinemia. By the reduction of \( \text{NO}_3^- \) to \( \text{NO}_2^- \), the ferrous ion is oxidized to ferric ions in the blood haemoglobin. In this stage oxygen becomes free and does not \( \text{Hb} \) to binding with the oxidized molecule (Bosch et al., 1950). Clinical signs of \( \text{NO}_3^- \) toxicity, attributable to hypoxia appear when methaemoglobin values exceed about 20% depending upon species susceptibility.
AMBIENT AIR LEVELS OF NITRATE

Nitrate aerosols are the final stage in the atmospheric oxidation of oxides of nitrogen \((\text{NO}_x)\) and substantial amounts of \(\text{P - NO}_3\) may be found in urban areas affected by photochemical pollution (Pitts and Lloyd, 1973). The concentration of nitrates in air may range from 1-40 kg/m\(^3\) depending upon the sampling and averaging periods. For eg. the estimated annual mean values (1968-1972) in Chattanooga, TN, USA were between 1 and 6 ug/m\(^3\) (French et al., unpublished). The daily mean concentrations of air-born nitrates in the central part of Tokyo ranged in 1973 from 0.9 to 41.8 kg/m with an annual mean of 8.2 mg/m. On the other hand in a small city with few industries (Matsue city) the daily means were in the range of 1.1 - 9.2 kg/m with an annual mean of 2.6 kg/m (Japan Environmental Sanitation Centre, 1974).

PARTICULATE NITRATE PATH IN AEROSOL

Current problems associated with the chemical and physical paths of the conversion of oxides of nitrogen and sulfur is the delineation. See
diagram 4 below for P - NO₃ path in aerosol.

1. Path one involves the formation of HNO₃ acid by homogeneous gas phase reactions involving NO and NO₂. HNO₃ once formed may then react with NH₃ to produce NH₄NO₃ or be absorbed directly into an aerosol droplet by paths 2 and 3.

2. Path 3 is unimportant when compared to other possible routes of incorporation of NO₃ in a across of particle. Path 4 involves the direct absorption of NO and NO₂ followed by chemical reactions within the droplet.

Path 6 involves the formation of organic nitrates through free radical reactions followed by absorption of these P - NO₃ into aerosol. See Diagram number 4.
P-NO₃ FORMATION MECHANISM IN AEROSOL OF ATMOSPHERE


DIAGRAM NO. 4
On a global scale, quantity of NO and NO2 produced naturally by bacterial and volcanic action and by lightning by far outweigh those generated by man's activities. However as they are distributed over the entire earth's surface, the resulting background atmospheric concentrations are very small. The major source of manmade emissions of NOx into the atmosphere is the combustion of fossil fuels, is stationary sources (heating, power generation) and motor vehicles (internal combustion engines). Other contributions to the atmosphere come from specific noncombustion industrial processes such as the manufacture of NO and explosives. Indoor sources, including smoking gas fired appliances, and oil stoves. Differences in the NO2 emission of various countries are mainly due to differences in fossil fuel consumption. World wide emissions of NOx in 1970 were estimated at approximately 53 million tonnes. See table Number 1.
TABLE - 1  CONTROLLED HUMAN STUDIES (No$_2$)

SENSORY EFFECTS

<table>
<thead>
<tr>
<th>Nitrogen dioxide concentration (ug/m)</th>
<th>Length of exposure</th>
<th>Effects</th>
<th>Response</th>
<th>Subjects</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>790</td>
<td>0.42</td>
<td>Odour perceived immediately after beginning of the exposure</td>
<td>8/8</td>
<td>8 healthy subjects</td>
<td>Henschler et al. 1960.</td>
</tr>
<tr>
<td>410</td>
<td>0.22</td>
<td>Odour perceived immediately after beginning of the exposure</td>
<td>8/13</td>
<td>13 healthy subjects</td>
<td>Henschler et al. 1960.</td>
</tr>
<tr>
<td>230</td>
<td>0.12</td>
<td>Odour perceived immediately after beginning of the exposure</td>
<td>8/13</td>
<td>13 healthy subjects</td>
<td>Henschler et al. 1960.</td>
</tr>
<tr>
<td>200</td>
<td>0.11</td>
<td>Odour perceived immediately after beginning of the exposure</td>
<td>26/28</td>
<td>28 healthy subjects</td>
<td>Feldman (1974)</td>
</tr>
<tr>
<td>0-51000</td>
<td>0-27 54 min</td>
<td>no odour perception when raising the concentration slowly within 54 min from 0 to 27 ppm; increase of relative humidity enhanced odour perception</td>
<td>0/6</td>
<td>6 healthy subjects</td>
<td>Henschler et al. (1960)</td>
</tr>
<tr>
<td>140</td>
<td>0.074 5 and 25 min</td>
<td>decreased dark adaptation in all subjects (nasal breathing)</td>
<td>4/4</td>
<td>4 healthy subjects</td>
<td>Salamberidze (1967)</td>
</tr>
</tbody>
</table>

aR = Response = number of subjects showing effects/total number of subjects
<table>
<thead>
<tr>
<th>Concentration</th>
<th>Time</th>
<th>Effect</th>
<th>Subjects</th>
</tr>
</thead>
<tbody>
<tr>
<td>9400</td>
<td>5</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>9400</td>
<td>5</td>
<td>1</td>
<td>15 min</td>
</tr>
<tr>
<td>9400</td>
<td>5</td>
<td>1</td>
<td>15 min</td>
</tr>
<tr>
<td>7500-9400</td>
<td>4-5</td>
<td>1</td>
<td>10 min</td>
</tr>
<tr>
<td>3000-3800</td>
<td>1.6-2.0</td>
<td>1</td>
<td>15 min</td>
</tr>
<tr>
<td>1300-3800</td>
<td>0.7-2.0</td>
<td>1</td>
<td>10 min</td>
</tr>
<tr>
<td>190</td>
<td>0.1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>100 in</td>
<td>0.05 in 1</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>combination</td>
<td>50</td>
<td>ozone and 0.025 ozone</td>
<td>and 0.10 sulfur dioxide</td>
</tr>
</tbody>
</table>

R = Airway resistance
SR = Specific airway resistance i.e. in the product of airway resistance and thoracic gas volume
AaDo = Alveolar to arterial oxygen pressure difference
DL = Diffusion capacity of the lung for carbon monoxide
PAO = Alveolar partial pressure of oxygen
PaO = Arterial partial pressures of oxygen
NO\textsubscript{x} REACTIONS IN THE ATMOSPHERE

A simplified reaction has been given for NO\textsubscript{x} in the presence of air pollutants such as RH etc.

\begin{align*}
2 \text{NO} + \text{O}_2 & \rightarrow 2\text{NO}_2 \\
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2
\end{align*}

(1) (2)

NO\textsubscript{2} absorbs strongly in the UV region between 300 and 400 um and is decomposed by sun-light yielding NO and O\textsubscript{3} (Leighton, 1961). Thus in daylight, reaction (2) proceeds in the opposite direction and eventually an equilibrium is established

\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2
\end{align*}

(3)

The air is more polluted in urban areas than in rural areas and the concentration of NO\textsubscript{x} is markedly higher. Particularly at night time, reaction (2) proceeds to completion and that all ozone is removed leaving substantial concentrations of both NO and NO\textsubscript{2} in the atmosphere. During the day, the equilibrium (3) shifts in favour of ozone formation. The pattern of NO\textsubscript{2} concentrations in urban air is therefore quite different from that of primary pollutants such as NO, CO, and SO\textsubscript{2}. The differences in behaviour between NO\textsubscript{2} and other primary pollutants show in the relationship between peak values and long term mean values, and in diurnal
and seasonal variability. In view of the effects on human health, conversion may have an added significance.

\[ \text{CH} + \text{NO}_2 \rightleftharpoons \text{HNO}_3 \]

A summary of controlled human studies which provide a quantitative basis for evaluating health risk from exposure to NO\(_2\).

There has been an increased awareness of the importance of NO\(_x\) in the atmosphere. The awakening interest is due to the mounting evidence of significant environmental impacts of NO\(_x\) (NO + NO\(_2\)) and its reaction products. Today, it appears that NO\(_x\) derived pollutants have detrimental effects on health, ecology (e.g., acidic precipitation) and our aesthetic enjoyment of surroundings (e.g., visibility reduction). The regular monitoring of NO\(_x\) particularly its major derived pollutant NO\(_2\) has given valuable insight into the chemical transformation and environmental hazards associated with oxidized nitrogen compounds in the atmosphere.

Non methane hydrocarbon (NMHC) and other organics shown here as NMOC (non methane organic compounds) and sun light to form a host of secondary pollutants. Some of these are criteria pollutants for example PAN, HNO\(_3\), HCHO and HCOOH. The overall reaction is

\[ \text{NMOC} + \text{NO}_x + \text{hv} \rightarrow \text{O}_3 \text{ PAN etc.} \]
SCHEMATIC DIAGRAM OF THE PROCESSES DETERMINING THE CONCENTRATION OF OZONE IN THE STRatosphere (FROM NATIONAL RESEARCH COUNCIL, 1982)

1. Earth

2. Troposphere

3, 4. Stratosphere

Solar UVRadiation down to 180 nm

Photolysis of \( \text{O}_2 \) initiates formation of \( \text{O}_3 \)

Slow transport, photodissociation of \( \text{O}_3 \)

Port removal of stratospheric \( \text{O}_3 \)

UV down to 290 nm, \( \text{HNO}_3 \) etc.

HCl removal of slow transport of \( \text{CCl}_4 \), \( \text{NO}_x \) etc.

Slow transport of \( \text{CCl}_4 \) and \( \text{N}_2\text{O} \)

Bulk circulation of \( \text{CCl}_4 \) store, \( \text{NO}_x \), etc.

Emission of \( \text{N}_2\text{O} \)

Diagram No. 5
OZONE AND TROPOSPHERE

It has been shown that pollution from the burning of fossil fuels contributes significantly to the ozone content in the troposphere. Tropospheric ozone through its absorption of infrared radiation is important for the earth heat budget. Oyestern (1984), because of polluting emissions. The greenhouse effect has been noted across the area of pollution where average temperatures in the troposphere are thought to have increased by about 0.2°C. Some climatologists predict a doubling of the concentration of tropospheric ozone over the course of the coming century, which could raise the surface temperature of the earth of nearly 1°C. Most of the solar ultraviolet radiation is absorbed by stratospheric ozone before it reaches the troposphere when approximately 10% of the atmospheric contents of ozone is found. The research on the distribution, formation, and destruction of atmospheric ozone has traditionally been focussed on the stratosphere. Advances in measurement techniques have made it possible to demonstrate that there is a pronounced variability in tropospheric ozone both in space and time. The variability is due to natural processes but anthropogenic impact also affects the distribution of and abundance of ozone.
It has become clear that ozone near the ground affects living systems in many ways and plays a very important role in numerous processes which impact on the chemical composition of the troposphere.

Exposure to enhanced ozone concentrations may pose a risk to the public health. In the US the ambient air quality standard for ozone is 120 ppbv, (parts per billion by volume) as an hourly mean, not to be exceeded more than once per year. There are indications that exposure to slightly enhanced ozone concentrations (e.g. 60 ppbv) during the growing season, may cause significant reductions in the yield of many crops. Enhanced ozone concentrations also indicate increased photochemical activity, pointing to efficient production of sulfates and nitrates in air rich in nitrogen oxides and sulfur dioxide of $SO_2$ to sulfate in the liquid phase through reaction with dissolved ozone contributes significantly to the sulfate levels found in precipitation.

Tropospheric ozone is very important for the infrared radiation budget of the atmosphere. The pressure broadening for ozone absorption causes the effective long wave optied depth of tropospheric ozone to be nearly the same as that of stratospheric ozone.
It has been calculated that doubling the tropospheric ozone content may increase the surface temperature by nearly 1°C, which is substantial compared to the 2-3°C temperature increase calculated for a doubling of CO₂. Refer diagram no. 5 determining the concentration of ozone in the stratosphere.