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# The Effects of Air Pollutants on Vegetation and the Role of Vegetation in Reducing Atmospheric Pollution

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## 1. Introduction

The main air pollutants are represented by gases forms, particles in suspension, different ionizing radiation and noise.

The gases forms are: oxidized and reduced forms of carbon ($CO_2$, $CO$, $CH_4$), of nitrogen ($NO_2$, $NO$, $N_2O_4$, $NH_3$, $NH^{4+}$), $SO_2$, $O_3$, $C_6H_6$ vapours, Hg, volatile phenols, $Cl_2$, etc.

The particulate forms are: PM10 and PM2.5 particulate matter, heavy metals with toxic effect (Pb, Ni, Cd, As), polycyclic aromatic hydrocarbons PAHs, etc.

Atmospheric pollutants have a negative effect on the plants; they can have direct toxic effects, or indirectly by changing soil pH followed by solubilization of toxic salts of metals like aluminum. The particulate matters have a negative mechanical effect. They cover the leaf blade reducing light penetration and blocking the opening of stomata. These impediments influence strongly the process of photosynthesis which rate declines sharply.

Also the leaves of the trees have an important role in retention of the particulate matters; they are mostly affected when the wet and dry atmospheric deposition increase.

The vegetation plays an important positive role in atmospheric purification and air pollutants reduction.

The primary producers represented by plants are an important component in biogeochemical cycles. The vegetation made exchanges with a part of the atmospheric gases by photosynthesis, respiration processes, and the final stage of litter decomposition which mineralization.

The plants play an important role in reducing atmospheric $CO_2$ content, by photosynthesis. This reduction of atmospheric $CO_2$ content has an important role in reducing of greenhouse gases, participating in reducing greenhouse effect and its consequences on climatic changes. The carbon stored in plants is the result of balance between carbon fixed by photosynthesis and carbon released in the atmosphere by respiration.

As the structure of vegetation is more complex, the carbon stock in plants biomass is higher and the period of storage is longer. The most efficient type of vegetation in storing carbon in terms of carbon stored in plants alive is the temperate-continental forest; and in terms of carbon stored in dead organic matter are peat lands.

Trees have also been planted to reduce the intensity of ionizing radiation and noise in different urban and industrial areas. The existence of vegetation in an area creates a microclimate where the temperature differentials between day and night are buffered.
This prevents the occurrence of warmer temperatures which stimulate the production of volatile pollutants into the atmosphere.

## 2. General information about air pollution

Environmental pollution is any discharge of material or energy into water, land, or air that causes or may cause acute (short-term) or chronic (long-term) detriment to the Earth's ecological balance or that lowers the quality of life. Pollutants may cause primary damage, with direct identifiable impact on the environment, or secondary damage in the form of minor perturbations in the delicate balance of the biological food web that are detectable only over long time periods.
Air pollution is the process which the substances and the energy forms are not present in normal atmospheric composition reach the atmosphere, or are present but in much lower concentrations.Air pollution is the introduction of chemicals, particulate matter, or biological materials that cause harm or discomfort to humans or other living organisms, or cause damage to the natural environment or built environment, into the atmosphere.
More than 3,000 substances that are not part of the atmospheric composition, falling in the atmosphere can be considered air pollutants.
Some substances that are normally present in the atmosphere in a certain concentration can be considerate pollutants because their concentration is much higher than usual concentration.
Also certain substances that are normally present in certain layers of the atmosphere (e.g. ozone in the stratosphere), once arrived in the troposphere is pollutant.
Some gases, such as oxides of nitrogen may have beneficial effect on vegetation, after hydration may affect the leaf fertilizer.
The air pollutants factors can be chemical (chemicals), mechanics (particles in suspension) physical (ionizing radiation) and acoustic (noise).

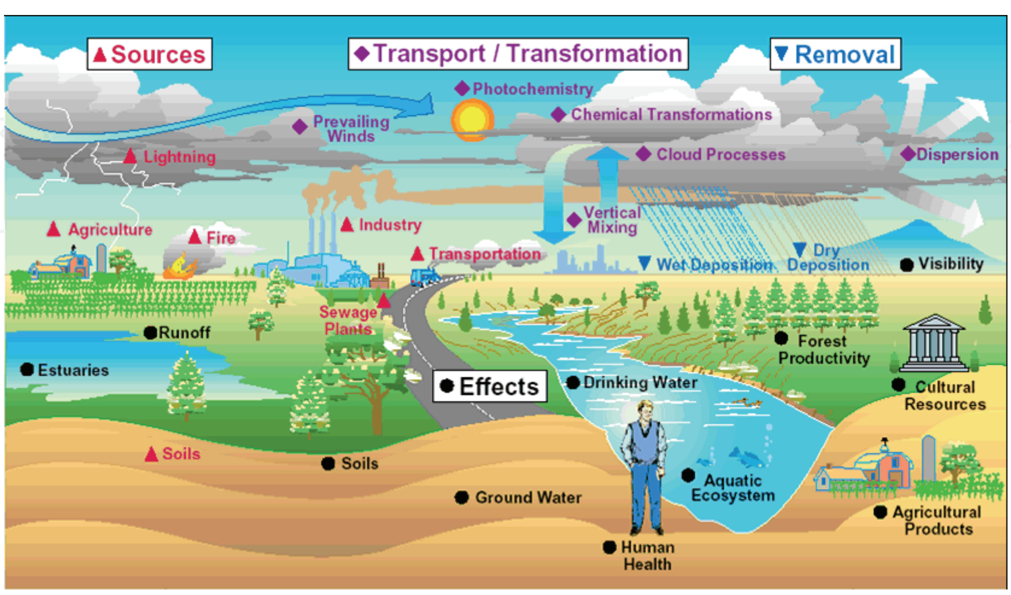

Fig. 1. Global polluants circuit (www.cleartheair.nsw.gov.au, 2011)

Pollutants describe a global circuit; they are produced by different sources, are transported and transformed into atmosphere, some of them being removed, another part is reaching the earth having different effects on different biocoenosis of ecosystems (fig. 1).

An analysis done at the global level revealed a diversification of pollutants agents and sources of air pollution. This diversification and increasing concentrations are in strict correlation with industrialization and the increasing of amounts use as fossil energy (non-renewable sources).

At the beginning, the pollution has been felt in urban areas and the forms of relief that favored the accumulation of pollutants and long stay (depressions, closed valleys, etc.). Currently, air pollution has become a larger area, sometimes to disperse across multiple continents.

Air pollution can be analyzed on three spatial scales: global pollution, regional pollution and local pollutants.

The global pollution is the result of cumulative effects of various sources, located on the entire surface of the globe, manifested by global effects: the stratospheric ozone depletion; greenhouse effect - emission of greenhouse gases ($CO_2$, methane, CFCs, etc.); formation of aerosols (pollutant clouds which suspended particles and chemical compounds).

The regional pollution is in part the result of local air pollution--including that produced by individual sources, such as automobiles - that has spread out to encompass areas of many thousands of square kilometers. Meteorological conditions and landforms can greatly influence air-pollution concentrations at any given place, especially locally and regionally. For example, cities located in bowls or valleys over which atmospheric inversions form and act as imperfect lids are especially likely to suffer from incidences of severe smog. Oxides of sulfur and nitrogen carried long distances by the atmosphere and then precipitated in solution as acid rain, can cause serious damage to vegetation, waterways, and buildings.

The local pollutants (smog) can be loosely defined as a multi-source, widespread air pollution that occurs in the air of cities. Smog, a contraction of the words smoke and fog, has been caused throughout recorded history by water condensing on smoke particles, usually from burning coal.

In terms of the effects of pollutants can be acidifying agents - sulphur dioxide ($SO_2$), nitrogen oxides (NOx) ammonia ($NH_3$) fluoride and $Cl_2$, hydrogen chloride (HCl) - and oxidizing agents - carbon monoxide (CO), PAN (peroxyacetylnitrate-$CH_3CO.O_2.NO_2$), ozone ($O_3$).

## 3. Sources of pollutants

Air pollution comes from natural and anthropic sources; these sources generate pollutants with different effects at global level or on individuals of plants and animals (tab. 1).

**Natural processes** that affect air quality include volcanoes, which produce sulfur, chlorine, and ash particulates. Wildfires produce smoke and carbon monoxide. Cattle and other animals emit methane as part of their digestive process. Even pine trees emit volatile organic compounds (VOCs).

Many forms of air pollution are **human-made**. Industrial plants, power plants and vehicles with internal combustion engines produce nitrogen oxides, VOCs, carbon monoxide, carbon dioxide, sulfur dioxide and particulates. In most mega-cities, cars are the main source of these pollutants. Stoves, incinerators, and farmers burning their crop waste produce carbon monoxide, carbon dioxide, as well as particulates. Other human-made sources include aerosol sprays and leaky refrigerators, as well as fumes from paint, varnish, and other solvents. One important thing to remember about air pollution is that it doesn't say in one place. Winds and weather play an important part in transport of pollution locally,

| Name of pollutants | Origin | Effects |
|---|---|---|
| Natural sources | | |
| sulfur, chlorine, and ash particulates, smoke and carbon monoxide methane volatile organic compounds (VOCs) Aerosol from deforestation and burning: $CO$, $CO_2$, $NO$, $NO_2$, $N_2O$, $NH_4$ | Volcanoes, wildfires, cattle and other animals, pine trees | - acid rain,<br>- smog,<br>- respiratory irritant<br>- increased respiratory<br>- diseases<br>- damage cell membranes of plants<br>The effects are high only for volcanoes. |
| Anthropic sources | | |
| Carbon monoxide, carbon dioxide, sulphur dioxide, nitrogen oxides, fluorides and substances with fluorine, chlorine ($Cl_2$), bromine ($Br_2$) and iodine ($I_2$), small dust particles, VOC, methane, ammonia and radioactive radiation. | Industry:<br>the mining industry, oil and natural gas extraction, the energy industry based on fossil fuels - coal, oil, natural gas, the production of brick, tile, enamel frit, ceramics, and glass; the manufacture of aluminium and steel; and the production of hydrofluoric acid, phosphate chemicals and fertilizers. central heating, chemical and metallurgical industry, engineering internal combustion machinery industry, industrial waste, noises | - respiratory irritant,<br>- acid rain,<br>- smog,<br>- increased respiratory<br>- formation of secondary pollutants (PAN, $O_3$)<br>- effect on soil fertilizer<br>- Respiratory diseases<br>- toxic effects on living cells<br>- greenhouse gas effect<br>- toxic effects<br>- carcinogenic proprieties<br>- accumulation in tissues<br>- blocking of different processes<br>- stratospheric ozone depletion |
| $CO$, $CO_2$, $NO$, $NO_2$, $NH_3$, $CH_4$, $SO_2$, oxides of heavy metals, $H_2SO_4$, SPM, HC, VOC, background aerosols: sea salt oxidation of sulphur containing gases, same organics, nitrous oxide ($N_2O$) pesticides | Agriculture:<br>the vegetation fire, the denitrification process, in soils excessively fertilized and excessive use the pesticides , paddy field, intensive husbandry, deforestation | - formation of secondary pollutants (PAN, $O_3$)<br>- effect on soil fertilizer<br>- respiratory diseases<br>- greenhouse gas effect<br>- toxic effects<br>- acid rain,<br>- stratospheric ozone depletion |
| Aerosols from transport and constructions $NO_x$, CO, HCl, Lead and other heavy metals , SPM | The motor vehicle pollution, noises | - smog<br>- increased respiratory diseases<br>- damage cell membranes of plants<br>- carcinogenic proprieties<br>- accumulation in tissues<br>- blocking of different processes<br>- stratospheric ozone depletion |
| Domestic aerosols CFC, HC, FC, $H_2S$, $CH_4$ $CO_2$ | sewage plans, authorized landfill site | - carcinogenic proprieties<br>- accumulation in tissues<br>- blocking of different processes<br>- stratospheric ozone depletion |

Table 1. Type of pollutants, origin and effect at global level or on plants end animals individuals

regionally, and even around the world, where it affects everything it comes in contact with. The major anthropic sources of air pollution are:

- industry and conventional energies (the mining industry, the energy industry based on fossil fuels - coal, oil, natural gas, central heating, chemical and metallurgical industry, engineering internal combustion machinery industry, industrial waste, noises, etc);

- agriculture (the vegetation fire, denitrification in soils excessively fertilized, paddy field, intensive husbandry, deforestation, etc)
- transportation (motor vehicle pollution, noises, etc)
- and urbanization (sewage plans, authorized landfill site, etc) (fig. 2)

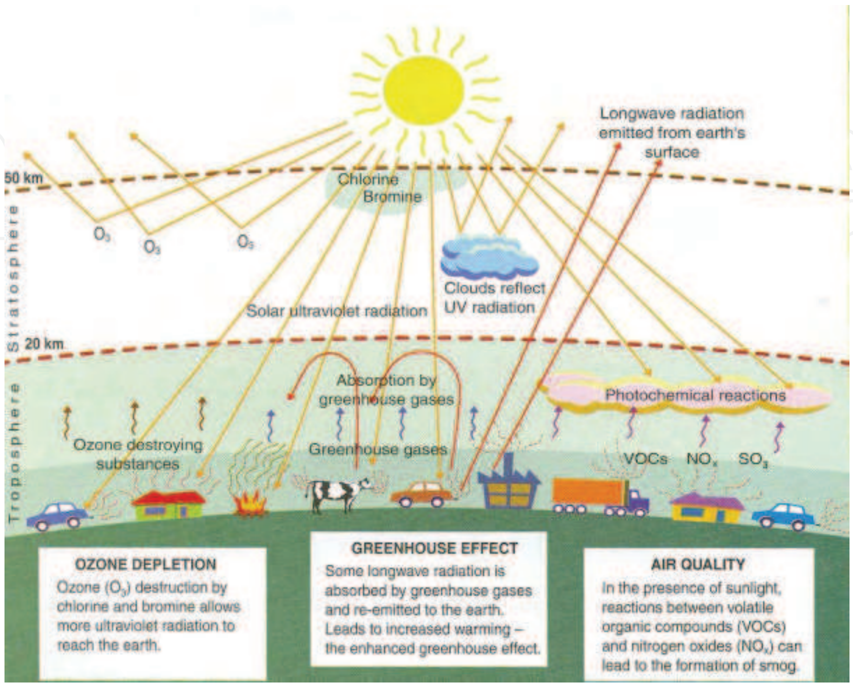


Fig. 2. The major anthropic sources of air pollution (www.cleartheair.nsw.gov.au, 2011)

## 4. The most important atmospheric pollutants

The air pollutants are represented by gases forms, particles in suspension, different ionizing radiation and noise.

## 5. Major gaseous pollutants

**Sulphur dioxide ($SO_2$)** is the most important and common air pollutant produced in huge amounts in combustion of coal and other fuels in industrial and domestic use. It is also produced during smelting of sulphide ores. Sulphur dioxide concentrations in air have decreased in the past two decades, mainly because we use more non-sulphur-containing fuels for the generation of energy. Sulphur dioxide is a stinging gas and as a result it can cause breathing problems with humans. In moist environments, sulphur dioxide may be transferred to sulphuric acid. This acid causes acidification and winter smog.
**Nitrogen oxides ($NO_x$) and nitrous oxide ($N_2O$)** Using catalysers in car exhausts can prevent emissions of nitrogen oxides. Nitrogen oxides are gasses that react with other air pollutants when they are present in air. For example, nitrogen oxides play an important rolein the formation of ozone in the lower atmosphere, and in acidification and eutrophication processes. They can deeply penetrate the lungs and damage human lung functions.
**Fluorides** Common gaseous fluoride pollutants are HF, $SiF_6$, $CF_4$ and $F_2$. Particulate fluoride pollutants include $Ca_3AlF_6$ (Cryolite), $CaF_2$, $NH_3F$, $AlF_6$, CaSiF, NaF and $Na_2SiF_6$. Aerosols are often formed from NaF, $NaAlF_6$ and $AlF_6$. Chief sources of fluoride pollutants are brickworks, aluminium factories, glassworks, steelworks, ceramic factories, phosphate

fertilizer plants and uranium smelters. Some fluorine pollution also occurs during combustion of coal. Most injurious fluoride pollutant is gaseous hydrogen fluoride (HF).
Fluoride is released into the air in large quantities by aluminum reduction plants, phosphate processors, steel mills, coal burning operations, brick and tile manufacturers, and various less significant sources[1]. It can cause adverse effects when ingested by domestic animals or absorbed by plants. There are also reports that fluoride air pollution can adversely affect human health, though these are less well documented than those concerning sensitive animals and plants. Fluorides are released into the air in both a gaseous state (as hydrogen fluoride and silicon tetra-fluoride) and in solid particles. The particles fall on, and the gases are absorbed by, vegetation near the polluting industry. If this vegetation includes forage crops which are fed to cattle, sheep, horses, or pigs, serious problems may ensue, since these animals, particularly the cattle are vulnerable to fluoride [2]. In fact, according to the U.S. Ninety-six percent of the ingested fluoride that accumulates in the bodies of animals is incorporated into the crystal structure of bone and tooth mineral [3], [4]. When fluoride is ingested with food or water, most of that which is not deposited in the bones, teeth, and other calcified tissue is excreted in the urine within hours of ingestion [5]. Thus it is not surprising that fluoride mainly affects the bones and teeth. Teeth are more markedly affected by ingested fluoride than are bones, but their high sensitivity is limited to the period of their formation. Thus a cow that has not been exposed to excessive fluoride before the age of two and one-half to three years will not develop the severe dental lesions which would occur in the same animal exposed at a younger age [6]. The developing tooth exposed to small amounts of fluoride may experience color variations ("mottling") that have little or no effect on the animal's ability to eat. Higher levels of fluoride result in more serious dental abnormalities, ranging from small, brittle, chalky areas on the tooth surface to pitting of enamel and easily eroded teeth [2]. Even more serious effects, including severe pain and the wearing down of the tooth right to the gum, can prevent the cattle from drinking cold water or eating. Localized or generalized enlargement of certain bones in the legs (metacarpals and metatarsals) and the lower jaw (mandible) of cattle are common symptoms of excessive fluoride ingestion [7]. As highly abnormal bone tissue replaces normal bone, [8] overall enlargement occurs, and the normally smooth bone surfaces take on a chalky, white, irregular appearance [2]. Hard ground can cause fluorotic hoof (pedal) bones to fracture, resulting in severe lameness [6]. Cattle with advanced fluorosis may also be crippled by mineralization of ligaments, tendons, and the structures surrounding the joints [9]. Enlargement of the joints themselves may also contribute to lameness. Fluoride-induced tooth destruction, lameness, and stiff joints affect the animal’s ability to stand, eat, and graze, and all tend to lower the milk yield of dairy cattle or the weight of beef cattle.
**Chlorine ($Cl_2$)** Although chlorine concentrations change very rapidly in the atmosphere due to atmospheric chemistry and light rain can remove all the chlorine from the air in a very short time, chlorine injury can occur to plants near the source of pollution.
The impact of chlorine pollution increases in bright sunlight and decreases in drought and low temperature.
Many particulate and gaseous fluorides are produced when ores containing fluorine are processed and used in industries. Common gaseous fluoride pollutants are HF, $SiF_6$, $CF_4$ and $F_2$. Particulate fluoride pollutants include $Ca_3AlF_6$ (Cryolite), $CaF_2$, $NH_3F$, $AlF_6$, CaSiF, NaF and $Na_2SiF_6$. Aerosols are often formed from NaF, $NaAlF_6$ and $AlF_6$. Chief sources of fluoride pollutants are brickworks, aluminium factories, glassworks, steelworks, ceramic factories, phosphate fertilizer plants and uranium smelters. Some fluorine pollution also occurs during combustion of coal. Most injurious fluoride pollutant is gaseous hydrogen fluoride (HF).

**Hydrogen chloride (HCl)** HCl gas is released in large quantities in combustion of PVC and all chlorinated hydrocarbon material in large fires or incinerators. The HCl gas is very hygroscopic and quickly changes to hydrochloric acid by reacting with atmospheric moisture and forms aerosol droplets.

**Ammonia ($NH_3$)** Continuous releases of ammonia from the sources are rarely high enough to cause acute injury but occasional high release or spillage may cause ammonia pollution. High concentrations of ammonia are sometimes found around intensive farm units e.g. chicken batteries. Extent of injury reduces rapidly with increase in distance form the source. Under certain conditions the ammonia may remain as a cloud above ground level causing more injury to trees than to the ground flora. Injury symptoms may take up to 9 days to develop. In most plant species, recovery may occur in about 2 weeks after exposure is stopped.

Ammonia forms during agricultural activities. EEA-32 emissions of $NH_3$ have declined by 24% between the years 1990 and 2008. Agriculture was responsible for 94% of $NH_3$ emissions in 2008. The reduction in emissions within the agricultural sector is primarily due to a reduction in livestock numbers (especially cattle) since 1990, changes in the handling and management of organic manures and from the decreased use of nitrogenous fertilizers. The reductions achieved in the agricultural sector have been marginally offset by the increased emissions which have occurred during this period in sectors such as transport and to a lesser extent the energy industry and other (non-energy) sectors.

Environmental context: $NH_3$ contributes to acid deposition (plays an important role in acidification) and eutrophication. The subsequent impacts of acid deposition can be significant, including adverse effects on aquatic ecosystems in rivers and lakes and damage to forests, crops and other vegetation. Eutrophication can lead to severe reductions in water quality with subsequent impacts including decreased biodiversity, changes in species composition and dominance, and toxicity effects. $NH_3$ also contributes to the formation of secondary particulate aerosols, an important air pollutant due to its adverse impacts on human health.

**VOC (Volatile Organic Compounds)** VOC can be a range of different contaminants, such as carbohydrates, organic compounds and solvents. These compounds usually derive from petrol and gasoline reservoirs, industrial processes and fuel combustion, paint and cleanser use, or agricultural activities. VOC play an important role in ozone shaping in the lower atmospheric layer, the main cause of smog. VOC can cause various health effects, depending on the kind of compounds that are present and their concentrations. Effects can vary from smell nuisance to decreases in lung capacity, and even cancer.

**Organic gases (Ethylene) and Methane ($CH_4$)** Among organic gaseous pollutants, ethylene is most common. Other organic gases are propylene, butylenes and acetylene. Ethylene is continuously emitted from many sources involving combustion or processing of petroleum or its products or burning of organic materials e.g. straw burning. Other organic gases are also produced in various chemical industrial processes.

Ethylene is a natural plant growth substance so the injury effects produced by it on plants are very similar to growth abnormality symptoms. Other organic gases also produce symptoms similar to those of ethylene pollution. However, the sensitivities of species to different gases are variable.

Ethylene is a byproduct of automobile exhaust and can be a noticeable problem in urban environments.

**Chlorofluorocarbons** (or CFCs) is an organic compound that contains carbon, chlorine, and fluorine, produced as a volatile derivative of methane and ethane. A common subclass is the **hydro-chlorofluorocarbons** (HCFCs), which contain hydrogen, as well. They are also commonly known by the DuPont trade name **Freon**. The most common representative is dichlorodifluoromethane (R-12 or Freon-12). Many CFCs have been widely used as refrigerants, propellants (in aerosol applications), and solvents. The manufacture of such compounds is being phased out by the Montreal Protocol because they contribute to ozone depletion.

**Minor gaseous pollutants** Many other air pollutants which are highly injurious to animals and human beings also cause damage to plants. However, plants are affected by these gases at quite higher concentrations than the animals. Common such gaseous pollutants are CO, $H_2S$, $Br_2$, $I_2$ and Hg - vapors.

**Hydrogen sulphide ($H_2S$)** It is a colorless, very poisonous, flammable gas with the characteristic foul odor of rotten eggs at concentrations up to 100 parts per million. It often results from the bacterial breakdown of organic matter in the absence of oxygen, such as in swamps and sewers (anaerobic digestion). It also occurs in volcanic gases, natural gas, and some well waters. The human body produces small amounts of $H_2S$ and uses it as a signaling molecule.

**Carbon monoxide** (CO) **carbon dioxide** in excess ($CO_2$), this gas consists during incomplete combustion of fuels. When we let a car engine run in a closed room, carbon monoxide concentrations in the air will rise extensively. Carbon monoxide contributes to the greenhouse effect, smog and acidification. The gas can bind to hemoglobin in blood, preventing oxygen transport through the body. This results in oxygen depletion of the heart, brains and blood vessels, eventually causing death.

It is highly toxic to humans and animals in higher quantities, although it is also produced in normal animal metabolism in low quantities, and is thought to have some normal biological functions.

Carbon monoxide consists of one carbon atom and one oxygen atom, connected by a triple bond which consists of two covalent bonds as well as one dative covalent bond. It is the simplest ox-carbon. In coordination complexes the carbon monoxide ligand is called carbonyl.

Carbon monoxide is produced from the partial oxidation of carbon-containing compounds; it forms when there is not enough oxygen to produce carbon dioxide ($CO_2$), such as when operating a stove or an internal combustion engine in an enclosed space. In the presence of oxygen, carbon monoxide burns with a blue flame, producing carbon dioxide [10]. Coal gas, which was widely used before the 1960s for domestic lighting, cooking and heating, had carbon monoxide as a significant constituent. Some processes in modern technology, such as iron smelting, still produce carbon monoxide as a byproduct [11]. Worldwide, the largest source of carbon monoxide is natural in origin; due to photochemical reactions in the troposphere which generate about $5 \times 10^{12}$ kilograms per year [12], other natural sources of CO include volcanoes, forest fires, and other forms of combustion.

In biology, carbon monoxide is naturally produced by the action of heme oxygenase 1 and 2 on the heme from hemoglobin breakdown. This process produces a certain amount of carboxyhemoglobin in normal persons, even if they do not breathe any carbon monoxide. Following the first report that carbon monoxide is a normal neurotransmitter in 1993, as well as one of three gases that naturally modulate inflammatory responses in the body (the other two being nitric oxide and hydrogen sulfide), carbon monoxide has received a great deal of clinical attention as a biological regulator . In many tissues, all three gases are known to act as anti- inflammatory, vasodilators and promoters of neo-vascular growth [13]. Clinical trials of small amounts of carbon monoxide as a drug are on-going.

**Bromine ($Br_2$) and Iodine ($I_2$)**

At high temperatures, organo-bromine compounds are easily converted to free bromine atoms, a process which acts to terminate free radical chemical chain reactions. This makes such compounds useful fire retardants and this is bromine's primary industrial use, consuming more than half of world production of the element. The same property allows volatile organo-bromine compounds, under the action of sunlight, to form free bromine atoms in the atmosphere which are highly effective in ozone depletion. This unwanted side-effect has caused many common volatile brominated organics like methyl bromide, a pesticide that was formerly a large industrial bromine consumer, to be abandoned. Remaining uses of bromine compounds are in well-drilling fluids, as an intermediate in manufacture of organic chemicals, and in film photography.

Iodine and its compounds are primarily used in nutrition, the production of acetic acid and polymers. Iodine's relatively high atomic number, low toxicity, and ease of attachment to organic compounds have made it a part of many X-ray contrast materials in modern medicine. Like the other halogens, iodine occurs mainly as a diatomic molecule $I_2$, not the atom. In nature, iodine is a relatively rare element, ranking 47th in abundance. It is the heaviest essential element utilized in biological functions. Its rarity in many soils has led to many deficiency problems in land animals and inland human populations, with iodine deficiency affecting about two billion people and being the leading preventable cause of mental retardation [14]. As a component of thyroid hormones, iodine is required by higher animals. Radioisotopes of iodine are concentrated in the thyroid gland. This property of thyroid-concentration, along with its mode of beta decay, makes iodine-131 one of the most carcinogenic nuclear fission products.

Hg and Mercury vapors Pre-industrial deposition rates of mercury from the atmosphere may be about 4 ng/ (1 l of ice deposit). Although that can be considered a natural level of exposure, regional or global sources have significant effects. Volcanic eruptions can increase the atmospheric source by 4–6 times [15]. Natural sources, such as volcanoes, are responsible for approximately half of atmospheric mercury emissions. The human-generated half can be divided into the following estimated percentages:

- 65% from stationary combustion, of which coal-fired power plants are the largest aggregate source (40% of U.S. mercury emissions in 1999). This includes power plants fueled with gas where the mercury has not been removed. Emissions from coal combustion are between one and two orders of magnitude higher than emissions from oil combustion, depending on the country [15].
- 11% from gold production. The three largest point sources for mercury emissions in the U.S. are the three largest gold mines. Hydro-geochemical release of mercury from gold-mine tailings has been accounted as a significant source of atmospheric mercury in eastern Canada [16]
- 6.8% from non-ferrous metal production, typically smelters.
- 6.4% from cement production.
- 3.0% from waste disposal, including municipal and hazardous waste, crematoria, and sewage sludge incineration. This is a significant underestimate due to limited information, and is likely to be off by a factor of two to five.

- 3.0% from caustic soda production.
- 1.4% from pig iron and steel production.
- 1.1% from mercury production, mainly for batteries.
- 2.0% from other sources [15], (EPA report, 2007).

The above percentages are estimates of the global human-caused mercury emissions in 2000, excluding biomass burning, an important source in some regions [15]. Current atmospheric mercury contamination in outdoor urban air is (0.01–0.02 $\mu g/m^3$) indoor concentrations are significantly elevated over outdoor concentrations, in the range 0.0065–0.523 $\mu g/m^3$ (average 0.069 $\mu g/m^3$) [17]. Mercury also enters into the environment through the improper disposal (e.g., land filling, incineration) of certain products.

## 6. Particulate pollutants

**Particles in suspension**

Dust particles. Dust particles form a complex of organic compounds and minerals. These can derive from natural sources, such as volcanoes, or human activities, such as industrial combustion processes or traffic. Particles are categorized according to particle size. The smallest particles have the ability to transport toxic compounds into the respiratory tract. Some of these compounds are carcinogenic. The upper respiratory tract stops the larger dust particles. When they are released into the environment, dust particles can cause acidification and winter smog.

**Cement-kiln dust** Cement factories are the chief source of cement dust pollution. The composition of such dust varies with the source. Main component of cement dust is CaO and varying amounts of $K_2O$, $Na_2O$ and KCl and traces of Al, Fe, Mn, Mg, S and silica. Dust with more than 24% CaO is more injurious to plants. Fine particles cause more damage than larger particles. Cement-kiln dust is alkaline in nature and dissolves in atmospheric moisture forming a solution of pH 10-12.

**Lime and gypsum** Lime and gypsum processing industries and mining deposits are chief sources from where fine particles of these substances are blown away to great distances.

**Soot** Burning of fossil fuels, organic matter or natural forest fires produce huge quantities of fine carbon particles which form the soot pollution. Soot can be dispersed over a quite wide area and transported to great distances by blowing winds.

**Magnesium oxide** Magnesium roasters are the chief sources of such pollution. The magnesium oxide dust may be carried by winds and deposited even at a distance of 5 km from the source. In the atmosphere, magnesium sulphate ($MgSO_4$) combines with carbon dioxide and water to form $Mg(CO_3)_2$. Both these compounds are alkaline and slightly soluble in water.

**Boron** Boric acid and borax are common raw materials in many industries. Oven and refrigerator manufacturing industries are chief sources of boron pollution.

**Chlorides of sodium, potassium and calcium** Sodium and calcium chlorides are commonly used in cold countries on the roads during winters to melt ice and snow. Potash industry produces aerial emission of KCl and NaCl in ratio of 3:1. All such chlorides are carried away by winds and deposited on the soil and plants.

**Sodium sulphate**, with an annual production of 6 million tones, it is a major commodity chemical and one of the most damaging salts in structure conservation: when it grows in the pores of stones it can achieve high levels of pressure, causing structures to crack.

Sodium sulfate is mainly used for the manufacture of detergents and in the Kraft process of paper pulping. About two-thirds of the world's production is from mirabilite, the natural mineral form of the decahydrate, and the remainder from by-products of chemical processes such as hydrochloric acid production.

**Pesticides, insecticides and herbicides** Pesticide use in the agricultural industry began in earnest in the early 1940s. Although pesticide use had been quite popular for more than twenty years, government officials first became aware of the potential danger of pesticide runoff to humans in the early 1960s when Rachel Carson's famous and influential *Silent Spring* was published. Though this book warned mainly of the detrimental effects of DDT (a popular insecticide developed in the early 1940s) for birds and other non-human victims, Carson's work inspired health officials to speculate about the effects of pesticide runoff on humans. Recently, exposure to DDT was linked to Parkinson's disease. Because of concern over DDT's adverse effects on the environment and on people, this pesticide was banned in 1972. Despite the ban of DDT, pesticide use continues, and the effects of some modern insecticides and herbicides can be just as debilitating. Even through careful use, runoff from pesticides continues to makes its way into drinking water sources.

## 7. Secondary pollutants

**Photo-oxidants** In presence of strong sunlight and in hot weather a series of complex chemical reactions involving nitrogen oxides and hydrocarbons may produce certain photo-oxidant chemicals. These chemicals do not have any specific anthropogenic source but are formed over wide areas in which suitable environmental conditions are prevailing. Two such photo-oxidants that can reach ambient concentrations toxic to plants are PAN (Peroxyacetylnitrate) and ozone.

**PAN (Peroxyacetylnitrate-$CH_3CO.O_2.NO_2$)** Impact of this secondary pollutant is not affected by humidity. However, the impact decreases with lowering of temperature and increasing drought conditions. The impact also increases in the morning and in bright sunlight. Young plants and young rapidly expanding leaves are more sensitive to this pollutant. PAN interacts with $SO_2$ and $O_3$ in complex manner producing variable impact conditions.

**Ozone ($O_3$)** is the main pollutant in the oxidant smog complex.

Ozone is formed in the troposphere when sunlight causes complex photochemical reactions involving oxides of nitrogen (NOx), volatile organic hydrocarbons (VOC) and carbon monoxide that originate chiefly from gasoline engines and burning of other fossil fuels. Woody vegetation is another major source of VOCs. NOx and VOCs can be transported long distances by regional weather patterns before they react to create ozone in the atmosphere, where it can persist for several weeks. Seasonal exposures at low elevations consist of days when ozone concentrations are relatively low or average, punctuated by days when concentrations are high. Concentrations of ozone are highest during calm, sunny, spring and summer days when primary pollutants from urban areas are present. Ozone concentrations in rural areas can be higher than in urban areas while ozone levels at high elevations can be relatively constant throughout the day and night.

Middle aged leaves and young plants are more sensitive to ozone. This pollutant interacts with $SO_2$, $NO_2$, PAN and heavy metals in complex manner.

Ozone is created through photochemical transfer of oxygen. This process takes place under the influence of ultra violet sunlight (UV), aided by pollutants in the outside air (fig. 2). Ozone causes smog and contributes to acidification and climate change. Ozone is an aggressive gas. This can easily penetrate the respiratory tract, deeply. When humans are exposed to ozone, the consequences may be irritation of the eyes and the respiratory tract.

**Acid deposition** Various acid gases, aerosols and other acidic substances released into the atmosphere from the industrial or domestic sources of combustion of fossil fuels eventually come down to the ground. These substances are deposited directly on the water bodies. In addition, these substances also reach the water bodies along with run-off rainwater from the polluted soil. Deposition of acidic substances causes acidification of water by lowering its pH below 6.0. The sulphates, nitrates and chlorides have been reported to make water bodies like lakes, rivers and ponds acidic in many countries.

Acid deposition is not merely characterized as acid rain; it can also be snow and fog or gas and dust. Acid deposition mainly forms during fossil fuel combustion. When emissions of sulphur dioxide and nitrogen oxides come in contact with water, they will become sulphuric acid and nitric acid.

When acidifying agents, such as sulphur dioxide, nitrogen oxides and ammonia, end up in plants, surface water and soils, this has a number of consequences:

- availability of nutrients and metal spores is likely to decrease
- when acidity is high more metals will dissolve in water. This can cause surface water to become polluted, which has serious health effects on aquatic plants and animals. For example, high aluminum (Al) concentrations can complicate nutrients uptake by plants. This makes aluminum one of the prior causes of forest decay. Mercury can be dispersed by transport through surface water, causing it to accumulate in fish. Mercury can bio magnify up the food chain, to be taken up by humans eventually
- Buildings and monuments may be damaged through erosion. Sulphur dioxide breaks down limestone by reacting with calcium carbonate, causing limestone to absorb water during rainfall. Limestone will than fragment

**Noise pollution** has a relatively recent origin. It is a composite of sounds generated by human activities ranging from blasting stereo systems to the roar of supersonic transport jets. Although the frequency (pitch) of noise may be of major importance, most noise sources are measured in terms of intensity, or strength of the sound field. The standard unit, one decibel (dB), is the amount of sound that is just audible to the average human. The decibel scale is somewhat misleading because it is logarithmic rather than linear; for example, a noise source measuring 70 dB is 10 times as loud as a source measuring 60 dB and 100 times as loud as a source reading 50 dB. Noise may be generally associated with industrial society, where heavy machinery, motor vehicles, and aircraft have become everyday items. Noise pollution is more intense in the work environment than in the general environment, although ambient noise increased an average of one dB per year during the 1980s. The average background noise in a typical home today is between 40 and 50 decibels. Some examples of high-level sources in the environment are heavy trucks (90 dB at 15 m/50 ft), freight trains (75 dB at 15 m/50 ft), and air conditioning (60 dB at 6 m/20 ft).

**Radiation pollution** is any form of ionizing or no ionizing radiation that results from human activities. The most well-known radiation results from the detonation of nuclear devices and the controlled release of energy by nuclear-power generating plants (see nuclear energy). Other sources of radiation include spent-fuel reprocessing plants, by-products of mining operations, and experimental research laboratories. Increased exposure to medical x rays and to radiation emissions from microwave ovens and other household appliances, although of considerably less magnitude, all constitute sources of environmental radiation.

**Radioactive radiation**. Radioactive radiation and radioactive particles are naturally present in the environment. During power plant incidents or treatments of nuclear waste from a war where nuclear weapons are used, radioactive radiation can enter the air on account of humans. When humans are exposed to high levels of radioactive radiation, the chances of serious health effects are very high. Radioactive radiation can cause DNA alteration and cancer.

## 8. Flow of atmospheric pollutants at global level

The air pollutants are produced by different sectors of the economy like: industry, agriculture, transports and urbanization. The burning of hydrocarbons in motor vehicle engines gives rise to $CO_2$, CO, $SO_2$ (sulfur dioxide), $NO_x$ (NO [nitrogen monoxide]) and $NO_2^-$- in varying proportions-and $C_2H_4$ (ethylene), as well as a variety of other hydrocarbons. Additional $SO_2$ originates from domestic and industrial burning of fossil fuels. Industrial plants, such as chemical works and metal-smelting plants, release $SO_2$, $H_2S$, $NO_2$, and HF (hydrogen fluoride) into the atmosphere. Tall chimney stacks may be used to carry gases and particles to a high altitude and thus avoid local pollution, but the pollutants return to Earth, sometimes hundreds of kilometers from the original source.

Photochemical smog is the product of chemical reactions driven by sunlight and involving $NO_x$ of urban and industrial origin and volatile organic compounds from either vegetation (*biogenic* hydrocarbons) or human activities (*anthropogenic* hydrocarbons). Ozone ($O_3$) and peroxyacetylnitrate (PAN) produced in these complex reactions can become injurious to plants and other life forms, depending on concentration and duration of exposure. Hydrogen peroxide, another potentially injurious molecule, can form by the reaction between $O_3$ and naturally released volatiles (terpenes) from forest trees.

The concentrations of polluting gases, or their solutions, to which plants are exposed are thus highly variable, depending on location, wind direction, rainfall, and sunlight. Experiments aimed at determining the impact of chronic exposure to low concentrations of gases should allow plants to grow under near-natural conditions. One method is to grow the plants in open-top chambers into which gases are carefully metered, or where plants receiving ambient, polluted air are compared with controls receiving air that has been scrubbed of pollutants.

These pollutants emitted into the atmosphere can react with components of the atmosphere and transform into more or less aggressive or toxic compounds. The air pollutants can accumulate and manifest directly effects in the atmosphere (greenhouse effect, ozone layer depletion, etc) or can to transform in other pollutants and manifest indirectly effects on ecosystem biocoenosis, plants, animals and human health (fig. 3)

## 9. Effect of pollutants on vegetation, direct effects, and indirect effect, gas toxicity, wet and dry deposition, and deposition mixtures

Dust pollution is of localized importance near roads, quarries, cement works, and other industrial areas. Apart from screening out sunlight, dust on leaves blocks stomata and lowers their conductance to $CO_2$, simultaneously interfering with photosystem II. Polluting gases such as $SO_2$ and $NO_x$ enter leaves through stomata, following the same diffusion pathway as $CO_2$. $NO_x$ dissolves in cells and gives rise to nitrite ions ($NO_2^-$, which are toxic at high concentrations) and nitrate ions ($NO_3^-$) that enter into nitrogen metabolism as if they had been absorbed through the roots. In some cases, exposure to pollutant gases,

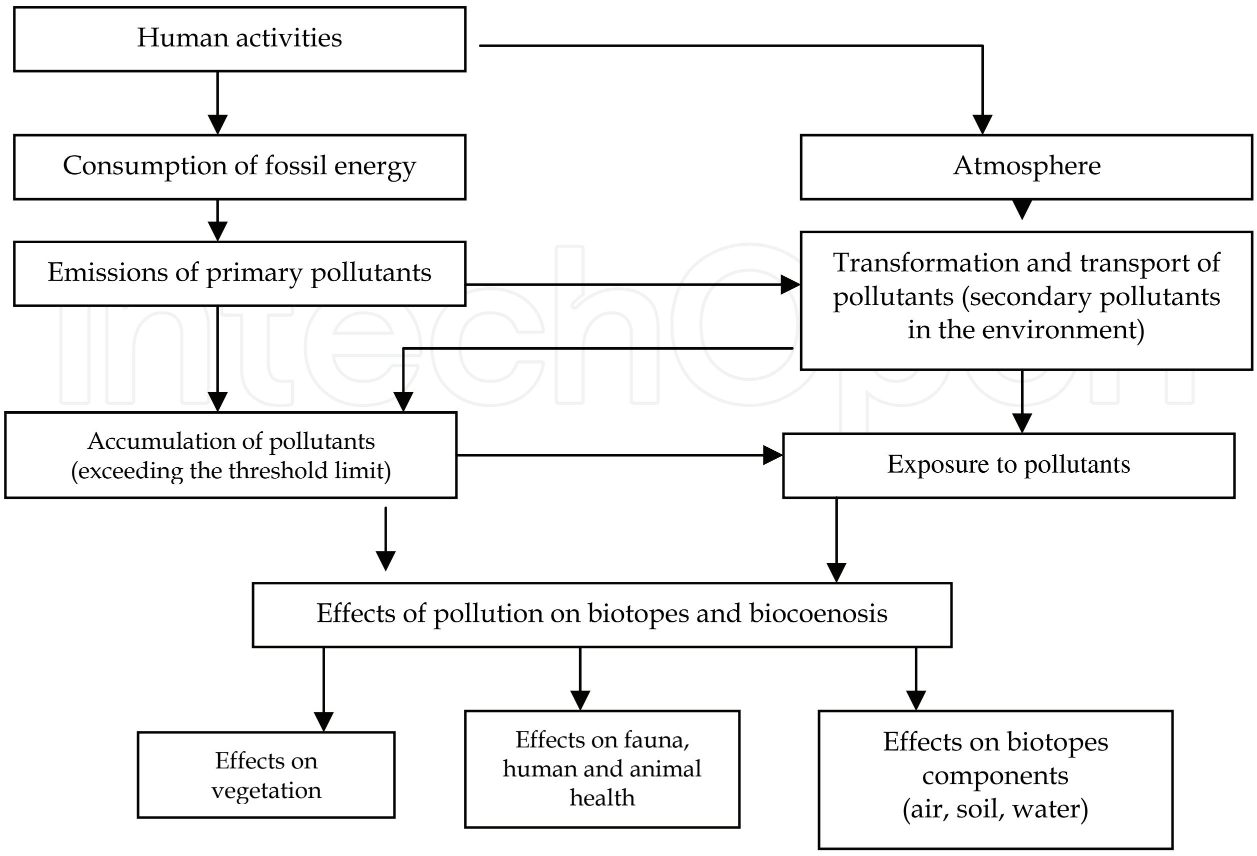


Fig. 3. The air pollutants flow diagram

particularly $SO_2$, causes stomatal closure, which protects the leaf against further entry of the pollutant but also curtails photosynthesis. In the cells, $SO_2$ dissolves to give bisulfite and sulfite ions; sulfite is toxic, but at low concentrations it is metabolized by chloroplasts to sulfate, which is not toxic. At sufficiently low concentrations, bisulfite and sulfite are effectively detoxified by plants, and $SO_2$ air pollution then provides a sulfur source for the plant. In urban areas these polluting gases may be present in such high concentrations that they cannot be detoxified rapidly enough to avoid injury. Ozone is presently considered to be the most damaging phytotoxic air pollutant in North America [18], [19]. It has been estimated that wherever the mean daily $O_3$ concentration reaches 40, 50, or 60 ppb (parts per billion or per $10^9$), the combined yields of soybean, maize, winter wheat, and cotton would be decreased by 5, 10, and 16%, respectively. Ozone is highly reactive: It binds to plasma membranes and it alters metabolism. As a result, stomatal apertures are poorly regulated, chloroplast thylakoid membranes are damaged, rubisco is degraded, and photosynthesis is inhibited. Ozone reacts with $O_2$ and produces reactive oxygen species, including hydrogen peroxide ($H_2O_2$), superoxide ($O_2^-$), singlet oxygen ($^1O_2^*$), and the hydroxyl radical ($^-OH$). These denature proteins and damage nucleic acids (thereby giving rise to mutations), and cause lipid peroxidation, which breaks down lipids in membranes. Reactive oxygen species form also in the absence of $O_3$, particularly in electron transport in the mitochondria and chloroplasts, when electrons can be donated to $O_2$. Cells are protected, at least in part, from reactive oxygen species by enzymatic and nonenzymatic defense mechanisms [20], [21]. Defense against reactive oxygen species is provided by the scavenging properties of molecules, such as ascorbic acid, α-tocopherol, phenolic compounds, and glutathione. Superoxide dismutases (SODs) catalyze the reduction of superoxide to hydrogen peroxide.

Hydrogen peroxide is then converted to $H_2O$ by the action of catalases and peroxidases. Of particular importance is the ascorbate-specific peroxidase localized in the chloroplast. Acting in concert, ascorbate peroxidase, dehydroascorbate reductase, and glutathione reductase remove $H_2O_2$ in a series of reactions called the *Halliwell–Asada pathway*, named after its discoverers. Glutathione is a sulfur-containing tripeptide that, in its reduced form, reacts rapidly with dehydroascorbate and becomes oxidized in the process. Glutathione reductase catalyzes the regeneration of reduced glutathione (GSH) from its oxidized form (GSSG) in the following reaction:

$$GSSG + NADPH + H^+ \rightarrow 2\,GSH + NADP^+$$

Exposure of plants to reactive oxygen species stimulates the transcription and translation of genes that encode enzymes involved in protection mechanisms. In Arabidopsis, exposure for 6 hours per day to low levels of $O_3$ induces the expression of several genes that encode enzymes associated with protection from reactive oxygen species, including SOD, glutathione S-transferase (which catalyzes detoxification reactions involving glutathione), and phenylalanine ammonia lyase (an important enzyme at the start of the phenylpropanoid pathway that leads to the synthesis of flavonoids and other phenolics) [22].

In transgenic tobacco transformed with a gene from *Escherichia coli* to give additional glutathione reductase activity in the chloroplast, short-term exposure to high levels of $SO_2$ is much less damaging than for wild-type tobacco [23]. Environmental extremes may either accelerate the production of reactive oxygen species or impair the normal defense mechanisms that protect cells from reactive oxygen species. In water-deficient leaves, for example, greater oxygen photoreduction by photosystems I and II increases superoxide production, and the pool of glutathione, as well as the activity of glutathione reductase, increase-presumably as part of the cell defense mechanism. In contrast, levels of ascorbate, another antioxidant, generally decline with mild water stress. Transgenic plants overexpressing mitochondrion superoxide dismutase (Mn-SOD), the isozyme localized in the mitochondrial matrix, show less water-deficit damage and, significantly, improved survival and yield under field conditions [24]. In other experiments, transgenic alfalfa overexpressing Mn-SOD was found to be more tolerant of freezing. Conversely, winter rye, wheat, and barley acclimated at 2 °C for several weeks, were found to have developed resistance to the herbicides, paraquat and acifluorfen, which generate reactive oxygen species. Such investigations support the hypothesis that tolerance of oxidative stress is an important factor in tolerance to a wide range of environmental extremes. Many deleterious changes in metabolism caused by air pollution precede external symptoms of injury, which appear only at much higher concentrations. For example, when plants are exposed to air containing $NO_x$, lesions on leaves appear at a $NO_x$ concentration of 5 ml/l, but photosynthesis starts to be inhibited at a concentration of only 0.1 ml/l. These low, threshold concentrations refer to the effects of a single pollutant. However, two or more pollutants acting together can have a synergistic effect, producing damage at lower concentrations than if they were acting separately. In addition, vegetation weakened by air pollution can become more susceptible to invasion by pathogens and pests. Unpolluted rain is slightly acidic, with a pH close to 5.6, because the $CO_2$ dissolved in it produces the weak acid, $H_2CO_3$. Dissolution of $NO_x$ and $SO_2$ in water droplets in the atmosphere causes the pH of rain to decrease to 3 to 4, and in southern California polluted droplets in fog can be as acidic as pH 1.7. Dilute acidic solution can remove mineral nutrients from leaves, depending on the age of the leaf and the integrity of the cuticle and surface waxes. The total annual contributions to the soil of acid from acid rain (*wet deposition*) and from particulate matter falling on the soil plus direct absorption from the atmosphere (*dry deposition*) may reach 1.0 to 3.0 kg $H^+$ per hectare in parts of Europe and the northeastern United States [25]. In soils that lack free calcium carbonate, and therefore are not strongly buffered, such additions of acid can be harmful to plants. Furthermore, the added acid can result in the release of aluminum ions from soil minerals, causing aluminum toxicity. Air pollution is considered to be a major factor in the decline of forests in heavily polluted areas of Europe and North America. There are indications that fast-growing pioneer species are better able to tolerate an acidifying atmosphere than are climax forest trees, possibly because they have a greater potential for assimilation of dissolved $NO_x$, and more effective acid buffering of the leaf tissue cell sap. Air pollution injury to plants can be evident in several ways. Injury to foliage may be visible in a short time and appear as necrotic lesions (dead tissue), or it can develop slowly as a yellowing or chlorosis of the leaf. There may be a reduction in growth of various portions of a plant. Plants may be killed outright, but they usually do not succumb until they have suffered recurrent injury.

Major primary air pollutants gases are sulphur dioxide, oxides of nitrogen particularly $NO_2$, HF, HCl, chlorine, ammonia, ethylene and other organic substances. Particulate air pollutants are soot, dust, fine particles of cement and various other substances. Various fertilizers, pesticides and insecticides used in aerial spray are also important air pollutants. The common sources of the pollutants, factors affecting the effect of pollutant and the injury symptoms produced in plants are discussed below.

## 10. Major gaseous pollutants

**Sulphur dioxide ($SO_2$)**

Sulfur dioxide is a major component in acid rain. One of the byproducts of sulfur dioxide is sulfuric acid, and both can be extremely damaging to plants that are exposed to these chemicals. Exposed leaves can begin to lose their color in irregular, blotchy white spots. Some leaves can develop red, brown or black spots. When the pigments in enough tissue are damaged or killed, plants can begin to lose their leaves. Crop output is greatly reduced and growth can be stunted. This is especially noticeable in young plants.

It is the most important and common air pollutant produced in huge amounts in combustion of coal and other fuels in industrial and domestic use. It is also produced during smelting of sulphide ores. Major sources of sulfur dioxide are coal-burning operations, especially those providing electric power and space heating. Sulfur dioxide emissions can also result from the burning of petroleum and the smelting of sulfur containing ores.

$SO_2$ effects increase in high humidity, windy conditions, in the early morning, in the deficiency of K and $Cl_2$ and excess of sulphur in the soil. It interacts with ozone, $NO_2$ and HF. The nature of interaction depends on the relative proportion of gases. The impact of $SO_2$ decreases in low soil moisture, low temperature, deficiency of nitrogen, sulphur and phosphorus and sometimes in excess of nitrogen also.

In angiosperms, young leaves and in conifers, needles are most sensitive to $SO_2$ pollution. In general, seedlings are more sensitive than older plants. The effect of the gas usually decreases with age of the plant and lesser morphological and physiological symptoms appear in older plants.

Injury symptoms: The gas is a strong reducing agent. In low concentration, it is oxidized and used in protein synthesis of the plant. However, in high concentration, it causes swelling of thylakoids and interferes with electron transport chain. In $SO_2$ pollution, plants show initial reduction of photosynthesis and increased respiration. The gas reduces stomatal opening and thus causes general water stress in plants. $SO_2$ replaces oxygen in cellular materials and changes their nature. It affects structural proteins in the cell membrane and thus changes the membrane permeability. High concentration of the gas causes accumulation of sulphydril and decrease of sulphides in plants. $SO_2$ interferes with amino acid metabolism and reduces the synthesis of proteins and enzymes. It stimulates the oxidation of PGA and increases the pentose phosphate cycle activity. It reduces the level of keto acids, ATP, sucrose and glutamate in plants and increases the level of glucose, fructose and glycolate. It inactivates many enzymes either by breaking their S-S bonds or by changing their stereo structure. In lichens, the gas induces photooxidation in the phycobiont part. Most common visible symptom of $SO_2$ injury is water-soaked appearance of leaves which later become necrotic changing into brown spots. Color and shape of necrotic spots is characteristic in different species and $NO_2$ concentrations. In some species, characteristic intraveinal chlorosis is caused. In general, $SO_2$ pollution results in abscission of older leaves and tip necrosis in flower and sepals.

Sulfur dioxide enters the leaves mainly through the stomata (microscopic openings) and the resultant injury is classified as either acute or chronic. Acute injury (fig. 4) is caused by absorption of high concentrations of sulfur dioxide in a relatively short time. The symptoms appear as 2-sided (bifacial) lesions that usually occur between the veins and occasionally along the margins of the leaves. The colors of the necrotic area can vary from a light tan or near white to an orange-red or brown depending on the time of year, the plant species affected and weather conditions. Recently expanded leaves usually are the most sensitive to acute sulfur dioxide injury, the very youngest and oldest being somewhat more resistant.

Fig. 4. Acute sulfur dioxide injuries to raspberry [26].

Chronic injury is caused by long-term absorption of sulfur dioxide at sub-lethal concentrations. The symptoms appear as a yellowing or chlorosis of the leaf, and occasionally as a bronzing on the under surface of the leaves. Different plant species and varieties and even individuals of the same species may vary considerably in their sensitivity to sulfur dioxide. These variations occur because of the differences in geographical location, climate, stage of growth and maturation. The following crop plants are generally considered susceptible to sulfur dioxide: alfalfa, barley, buckwheat, clover, oats, pumpkin, radish, rhubarb, spinach, squash, Swiss chard and tobacco. Resistant crop plants include asparagus, cabbage, celery, corn, onion and potato. Plants damaged by sulfur dioxide can be as far as 30 miles from its source, but the most severe damage, defoliation and discoloring is typically found within five miles. For some plants, it can take exposure of only four hours to suffer damage. A wide variety of plants are vulnerable, from alfalfa and carrots to crab apple and fir trees.

**Nitrogen dioxide ($NO_2$)**

$NO_2$ mostly affects the leaves and seedlings. Its effects decrease with increasing age of the plant and tissue. Conifers are found to be more sensitive to this gas during spring and summer than in winters. Older needles are more sensitive to the gas than young ones.

Injury symptoms: The gas causes formation of crystalloid structures in the stroma of chloroplasts and swelling of thylakoid membrane. As a result the photosynthetic activity of the plant is reduced.

Most common visible injury symptoms are chlorosis in angiospermic leaves and tip burn in conifer needles. In angiosperms, most of the species produce water-soaked intraveinal areas that later become necrotic. Tip burn is common symptom in bracts, sepals and awns.

**Fluorides**

Fluirides in general, are accumulated in the plant tissues over long times. They are first accumulated in the leaves and then are translocated towards tips and margins of the leaves. The injury symptoms are produced only after a critical level of fluoride is attained. Due to such accumulation over long times, flurides generally and HF particularly can induce injury at very low atmospheric concentrations. Critical concentration for fluoride injury is 0.1 ppm for several days. Toxicity of particulate fluorides depends upon the particle size, their solubility and humidity of the atmosphere.

HF gas is much lighter than air and so can cause damage in plants even at a distance of 30 km from the source. It is a hygroscopic gas and forms acidic cloud near the source. Generally the impact of HF pollution increases with humidity and excess of P in soil while decreases in low temperature, drought and deficiency of N and Ca in the soil. In some species, impact of HF has been reported to decrease with excess of N and Ca in the soil.

In most of the species, recovery from moderate fluoride injury can occur within few days if exposure to pollutant stops. However, some highly sensitive species e.g. pine and spruce can never recover fully. HF generally affects immature leaves in angiosperms and needles in conifers.

Injury symptoms: Fluorides combine with metal components of proteins or inhibit them otherwise and thus interfere with the activity of many enzymes. As a result the cell wall composition, photosynthesis, respiration, carbohydrate synthesis, synthesis of nucleic acids and nucleotides and energy balance of the cell are affected. In the leaves subjected to HF exposure, endoplasmic reticulum is reduced, ribosomes are detached from ER, number of ribosomes is reduced and mitochondria become swollen. Chlorophyll synthesis and cellulose synthesis are inhibited. Activities of UDP-glucose-fructose transglucosylase, phosphoglucomutase, enolase and polyphenol oxidase are reduced. On the other hand activities of catalase, peroxidase, pyruvate kinase, PEP-carboxylase, glucose-6-phosphate dehydrogenase, cytochrome oxidase and pentose phosphate pathway are stimulated. In conifer needles common visible injury symptoms are chlorosis later turning into red/brown discolouration, tip burn later turning into necrosis of whole needle, formation of sharply defined red/purple bands between healthy and injured tissue. Similar symptoms are common in angiospermic leaves also. In addition, the angiospermic leaves in many species also show zonation of necrotic areas, leaf cupping, curling of leaf edges and ragged leaf margins. In sepals, petals, bracts and awns, water-soaked margins and later tip and marginal necrosis are observed. Fluorides absorbed by leaves are conducted towards the margins of broad leaves (grapes) and to the tips of monocotyledonous leaves (gladiolus).

Little injury takes place at the site of absorption, whereas the margins or the tips of the leaves build up injurious concentrations. The injury (fig. 5) starts as a gray or light-green water-soaked lesion, which turns tan to reddish-brown. With continued exposure the necrotic areas increase in size, spreading inward to the midrib on broad leaves and downward on monocotyledonous leaves.

Fig. 5. Fluoride injuries to plum foliage [26].

The fluoride enters the leaf through the stomata and is moved to the margins where it accumulates and causes tissue injury. Note, the characteristic dark band separating the healthy (green) and injured (brown) tissues of affected leaves. Studies of susceptibility of plant species to fluorides show that apricot, barley (young), blueberry, peach (fruit), gladiolus, grape, plum, prune, sweet corn and tulip are most sensitive. Resistant plants include alfalfa, asparagus, bean (snap), cabbage, carrot, cauliflower, celery, cucumber, eggplant, pea, pear, pepper, potato, squash, tobacco and wheat.

**Chlorine ($Cl_2$)**

Older plants are more sensitive to chlorine than seedlings. The age of tissue has little effect on the sensitivity and older as well as young tissues are almost equally afected by chlorine pollution.

Injury symptoms: Chlorine injury symptoms can appear from 18 hours to 8 days after exposure. In most plant species, recovery from chlorine injury can occur 3 to 4 days after exposure is stopped. Chlorine injury symptoms are quite variable in different species. Most common visible symptoms in conifers are chlorosis, tip burn and necrosis is needles. In angiosperm leaves, marginal or intraveinal necrosis, water-soaked appearance, leaf cupping and abscission are common.

**Hydrogen chloride (HCl)**

The HCl injury can be caused to plants even at a distance of 800 meter from the source. Like fluorides, the chloride from HCl is accumulated in the leaves and translocated towards their margins and tips. Symptoms of HCl injury appear after a critical concentration is reached, usually between 24 and 72 hours after the exposure.

Impact of HCl pollution decreases with increase in humidity, deficiency of Mg and excess of Ca. Mature plants are more sensitive to HCl than seedlings. Similarly, young fully expanded leaves are more sensitive than immature unexpanded leaves.

Injury symptoms: Most common visible injury symptoms in conifer needles are red or brown discolouration and tip burn. In angiosperm leaves, common symptoms are intraveinal water-soaked streaks, yellow or brown necrosis, tip necrosis, bleached areas around the necrosis and shot-holing. Tip burn, necrotic stipple and discolouration in sepals and petals are also observed.

**Ammonia ($NH_3$)**

Impact of ammonia on plants generally increases with humidity and decreases with drought. Effect of darkness on ammonia sensitivity is highly variable among species. Some species are more sensitive to low concentrations of ammonia than to its high concentration. Age of tissue has little effect on sensitivity and both young and old tissues are equally sensitive to ammonia.

Injury symptoms: Most common visible symptoms in conifers are black discolouration, usually sharply bordered tip burn and abscission of needles. In angiosperm leaves, common symptoms are water-soaked appearance later turning black, intercostal necrosis, slight marginal and upper surface injury, glazong/bronzing of upper surface, desiccation and abscission. Ammonia injury to vegetation has been observed frequently in Ontario in recent years following accidents involving the storage, transportation or application of anhydrous and aqua ammonia fertilizers. These episodes usually release large quantities of ammonia into the atmosphere for brief periods of time and cause severe injury to vegetation in the immediate vicinity. Complete system expression on affected vegetation usually takes several days to develop, and appears as irregular, bleached, bifacial, necrotic lesions. Grasses often show reddish, interveinal necrotic streaking or dark upper surface discolouration. Flowers, fruit and woody tissues usually are not affected, and in the case of severe injury to fruit trees, recovery through the production of new leaves can occur (fig. 6). Sensitive species include apple, barley, beans, clover, radish, raspberry and soybean. Resistant species include alfalfa, beet, carrot, corn, cucumber, eggplant, onion, peach, rhubarb and tomato.

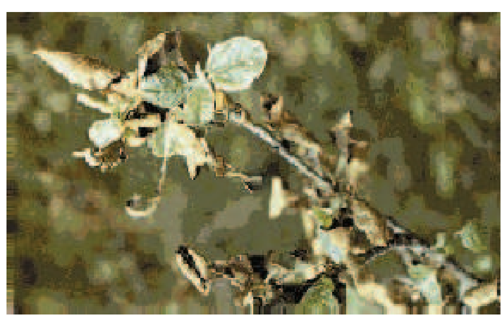

Fig. 6. Severe ammonia injuries to apple foliage and subsequent recovery through the production of new leaves following the fumigation [26].

**Organic gases (Ethylene)**

Ethylene injury symptoms develop in plants only in exposure to high concentrations and take several days to develop. After exposure to the gas is stopped, level of recovery is variable in different species. Generally, younger plant parts recover but older parts do not. Much 'acute' damage to plants is caused on the fringes of polluted area or by a steady leakage of gas in low concentration.

Injury symptoms: In injuriously high concentrations of ethylene, growth of plants is stopped. In low concentrations, growth abnormalities appear. In conifers, yellow tips in needles and abscission of branches and cones are common. In angiosperms, common symptoms are epinasty or hyponasty, loss of bark, abscission of leaves and flowers, premature flower opening and fruit ripening. Ethylene affects the growth hormones and regulatory process that takes place in the plant and results in a number of outward manifestations of infection. Leaves can begin to curl and die; ethylene causes the leaves of plants to curl down and fold under as they shrivel and are stuck with necrosis. On flowering plants, buds can stop opening or flowers can begin to show signs of discoloration or die and drop sooner than expected. Even in more resistant plants like evergreen conifers, growth of the plant will be stunted, needles will be small and few pine cones will be produced. Plants such as peach trees, marigolds, blackberries and tomatoes are extremely vulnerable to damage from exposure to ethylene.

## 11. Minor gaseous pollutants

**Hydrogen sulphide ($H_2S$)**
Plants show wilting on exposure to this gas but the symptoms develop after about 48 hours. No injury occurs below the exposure of 40 ppm for 4 hours.
**Carbon monoxide (CO)**
Like ethylene this gas produces epinasty, chlorosis and abscission. However, concentration of over 1000 times that of ethylene is needed to produce same degree of damage. No injury to plants occurs below exposure of 100 ppm for 1 week.
**Bromine ($Br_2$) and Iodine ($I_2$)**
Studies show these gases are highly toxic to plants. HI and $I_2$ are readily absorbed and accumulated by plants producing visible injury symptoms similar to those of $SO_2$. Injury occurs at exposure of 0.1 ppm for 18 hours.
Common injury symptoms of bromine in angiosperms are necrosis of leaf margins, leaf tips and tendrils; brown discoloration and black spots later spreading to entire leaf. In conifers, yellow/white needle tips or red/brown discoloration later becoming grey/brown are common symptoms.
**Mercury vapors (Hg)**
Unlike other pollutants, flowers are more sensitive to Hg than leaves. Injury symptoms usually appear within 24 hours of Hg exposure but often go on increasing up to 5 days.
Common injury symptoms due to Hg-vapors pollution are abscission of oldest leaves, interveinal necrosis, chlorosis around veins, flower abscission, loss of petal colors, buds remaining closed and later becoming necrotic, blackening of stamens, pistils and peduncles.
**Particulate pollutants**
Different types of solid particulate materials are also important air pollutants. Each of these affects the plants in characteristic manner. Some common particulate air pollutants have been discussed below.
**Cement-kiln dust**
In generals, plants having hairy surface of leaves trap more dust and are, therefore, damaged more than the plants with shiny leaf surface. The cement dust forms crusts on the surface of leaves, twigs and flowers. This inhibits gaseous exchange from the surfaces of plant parts. Such crust on the leaves also inhibits light penetration and consequently reduces photosynthesis. Such crusts are especially thicker in conditions of dew, mist or light rains. In dry conditions, dust blowing with wind is highly abrasive and damages the cuticle of leaves. Cuticle is also damaged due to alkalinity of cement dust. Due to damaged cuticle plants become more susceptible to infection by pathogens.
**Lime and gypsum**
Lime and gypsum deposited on the soil from the air, these change the pH of the soil and thus affect the nutrient availability to plants. Such deposition usually causes appearance of various nutrient deficiency symptoms in the plants. Lime and gypsum are less adhering as compared to cement-kiln dust. However, these are also trapped and deposited on the

surface of plant parts particularly the leaves with hairy surfaces and produce injury symptoms similar to cement dust. Lime and gypsum particles blowing with wind are also highly abrasive for cuticle.

**Soot**

Soot deposited on the surface of leaves may be washed away by rains so its damage may be reduced. However, in bright sunlight and high temperature, the damage is increased.

Soot deposited on the surface of leaves inhibits light penetration, increased surface temperature due to absorption of heat and clogging of stomata. The result of these is reduced gaseous exchange, reduced photosynthesis and general weakening of the plant growth. Necrotic spots also develop in many species due to soot deposition.

**Magnesium oxide**

Deposited on the soil these compounds can soon increase the soil pH to levels injurious to plants. Deposition of these substances on the soil prevents germination of seedlings. The seedlings that are able to emerge usually have yellow/brown tips of leaves and their roots are stunted. In areas of heavy pollution, composition of the vegetation changes completely.

**Boron**

Severe injury to plants is observed even at a distance of 200 meters from the source and mild injury may be observed up to 500 meters in all the directions from the source.

Impact of boron pollution is more severe on older leaves than on younger leaves. Boron is also accumulated in the leaves and produces injury symptoms quite similar to fluoride pollution.

**Chlorides of sodium, potassium and calcium** Injury symptoms produced by these chlorides in plants are very similar to those produced by $SO_2$ and fluoride pollution.

**Sodium sulphate** dust can cause necrosis of leaves of the plants. The damage increases in moist condition.

**Pesticides, insecticides and herbicides**

A large variety of such chemicals are sprayed on the crops these days. These substances may drift with wind to nearby areas. Generally, these chemicals are deposited on the soil and form important soil pollutants. However, in frosty conditions when crops and other plants damaged by early frost are quite susceptible to foliar spray of these chemicals, these may also be injurious air pollutants. Injury symptoms vary with the plant species and the type of chemical. Generally, the symptoms are produced on foliage and are quite similar to those produced when these substances act as soil pollutants.

## 12. Secondary pollutants and plants

Many of the primary pollutants under specific environmental conditions may interact with each other and produce secondary environmental pollutants or certain complex environmental conditions that are injurious to plants. Such secondary pollutants and pollution conditions are discussed below.

**Photo-oxidants**

**PAN (Peroxyacetylnitrate-$CH_3CO.O_2.NO_2$)**

The common visible symptoms of exposure to PAN are chlorosis and necrosis in leaves. It also interferes with photosynthesis, respiration and absorption and synthesis of carbohydrates and proteins. It inhibits photorespiration, NADP reduction, carbon dioxide fixation, cellulose synthesis and the enzymes associated with photosynthesis and respiration.

**Ozone ($O_3$)** is released into the atmosphere from the burning of fossil fuels and is one of the most harmful pollutants to plants. It can be carried for long distances and is readily absorbed as a part of the photosynthetic process. Plants exposed to large amounts of ozone can develop spots on their leaves. These spots are irregular and often tan, brown or black. Some leaves can take on a bronze or red appearance, usually as a precursor to necrosis. Depending on the concentration of ozone in the environment, plants can show different amounts of discoloration before the leaves begin to die.
Studies by the National Crop Loss Assessment Network show that ozone in the environment also has a detrimental effect on crop production. While crops such as cotton, soybeans and other dicots are more sensitive than monocot crops, all crops sampled over the decades-long studies show significant loss of productivity when exposed to ozone. Cotton crops show significantly less yield when exposed to levels of ozone in the atmosphere. Middle aged leaves and young plants are more sensitive to ozone. This pollutant interacts with $SO_2$, $NO_2$, PAN and heavy metals in complex manner.
Common symptoms of ozone pollution are yellowing, flecking and blotching in leaves, premature senescence and early maturity. It interferes with pollen formation, pollination, pollen germination and growth of pollen tubes. Increase in the level of RNA, starch, polysaccharides and number of polysomes is observed in ozone pollution. Ozone stimulates respiration, inhibits oxidative phosphorylation and changes membrane permeability. In some species, it inhibits the synthesis of glucon and cellulose and reduces the level of reducing sugars, ascorbic acid and ATP while in other species the effect is opposite to it. The impact of ozone on plants increases with humidity and decreases with drought, darkness, low temperature, high soil salinity, deficiency of soil phosphorus and excess of soil sulphur. Throughout the growing season, particularly July and August, ozone levels vary significantly. Periods of high ozone are associated with regional southerly air flows that are carried across the lower. Localized, domestic ozone levels also contribute to the already high background levels. Injury levels vary annually and white bean, which are particularly sensitive, are often used as an indicator of damage. Other sensitive species include cucumber, grape, green bean, lettuce, onion, potato, radish, rutabagas, spinach, sweet corn, tobacco and tomato. Resistant species include endive, pear and apricot.

Fig. 7. Ozone injuries to soybean foliage [26].

Ozone symptoms (fig. 7) characteristically occur on the upper surface of affected leaves and appear as a flecking, bronzing or bleaching of the leaf tissues. Although yield reductions are usually with visible foliar injury, crop loss can also occur without any sign of pollutant stress.

Conversely, some crops can sustain visible foliar injury without any adverse effect on yield. Susceptibility to ozone injury is influenced by many environmental and plant growth factors. High relative humidity, optimum soil-nitrogen levels and water availability increase susceptibility. Injury development on broad leaves also is influenced by the stage of maturity. The youngest leaves are resistant. With expansion, they become successively susceptible at middle and basal portions. The leaves become resistant again at complete maturation

Ground-level ozone causes more damage to plants than all other air pollutants combined. This web page describes the ozone pollution situation, shows classical symptoms of ozone injury and shows how ozone affects yield of several major crops.

Ozone enters leaves through stomata during normal gas exchange. As a strong oxidant, ozone (or secondary products resulting from oxidation by ozone such as reactive oxygen species) causes several types of symptoms including chlorosis and necrosis. It is almost impossible to tell whether foliar chlorosis or necrosis in the field is caused by ozone or normal senescence. Several additional symptom types are commonly associated with ozone exposure, however. These include flecks (tiny light-tan irregular spots less than 1 mm diameter), stipples (small darkly pigmented areas approximately 2-4 mm diameter), bronzing, and reddening.

Ozone symptoms usually occur between the veins on the upper leaf surface of older and middle-aged leaves, but may also involve both leaf surfaces (bifacial) for some species. The type and severity of injury is dependent on several factors including duration and concentration of ozone exposure, weather conditions and plant genetics. One or all of these symptoms can occur on some species under some conditions, and specific symptoms on one species can differ from symptoms on another. With continuing daily ozone exposure, classical symptoms (stippling, flecking, bronzing, and reddening) are gradually obscured by chlorosis and necrosis.

Studies in open-top field chambers have repeatedly verified that flecking, stippling, bronzing and reddening on plant leaves are classical responses to ambient levels of ozone. Plants grown in chambers receiving air filtered with activated charcoal (CF) to reduce ozone concentrations do not develop symptoms that occur on plants grown in non-filtered air (NF) at ambient ozone concentrations. Foliar symptoms shown on this web site mainly occurred on plants exposed to ambient concentrations of ozone (either in NF chambers or in ambient air).

**Yield Loss Caused by Ozone**

Field research to measure effects of seasonal exposure to ozone on crop yield has been in progress for more than 40 years. Most of this research utilized open-top field chambers in which growth conditions are similar to outside conditions. The most extensive research on crop loss was performed from 1980 to 1987 at five locations in the USA as part of the National Crop Loss Assessment Network (NCLAN). At each location, numerous chambers were used to expose plants to ozone treatments spanning the range of concentrations that occur in different areas of the world. The NCLAN focused on the most important agronomic crops nationally

The strongest evidence for significant effects of ozone on crop yield comes from NCLAN studies [18] (fig. 8). The results show that dicotyledonous species (soybean, cotton and peanut) are more sensitive to yield loss caused by ozone than monocot species (sorghum, field corn and winter wheat).

**Particulate Matter**

Particulate matter such as cement dust, magnesium-lime dust and carbon soot deposited on vegetation can inhibit the normal respiration and photosynthesis mechanisms within the leaf. Cement dust may cause chlorosis and death of leaf tissue by the combination of a thick crust and alkaline toxicity produced in wet weather. The dust coating (fig. 9) also may affect the normal action of pesticides and other agricultural chemicals applied as sprays to foliage. In addition, accumulation of alkaline dusts in the soil can increase soil pH to levels adverse to crop growth.

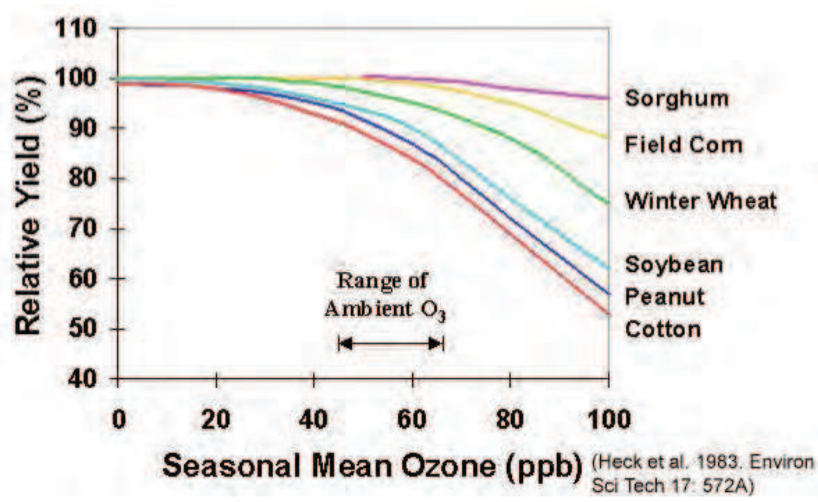


Fig. 8. Effect of ozone on yield of crops [18]. cotton image by arklite06 from

Fig. 9. Cement-dust coating on apple leaves and fruit. The dust had no injurious effect on the foliage, but inhibited the action of a pre-harvest crop spray [26].

## 13. Effect of atmospheric pollutants on vegetation monitoring system, why forestry monitoring system?

Because the crop plants are mostly annual plants they can not show the long-term effects produced by air pollutants. Therefore to monitor the effects of air pollution are recommended the trees, the changes in forest structure highlight the harmful effects of different air pollutants.

The evident decline of the health state of the forest in Europe since the beginning of the 1980 due to the negative impact of air pollution were illustrated by numerous publication from this period (see litt.). In the efforts to obtain objective and comparable data concerning the health of the European forests were developed a common methodology for the assessment of the forest state under the influence of air pollution. This network is known under the short term ICP- Forest (International Cooperative Programme for the investigation of the trans-boundary Pollution Influence on the Forests).

The poor health status of the forests in Central Europe concerns all the Europe. The pictures of the forests on large area were dominated by tree with defoliated crowns and an increasing rate of the death trees (fig 10). The assessment of the causes of the "new damages"- neuartiges waldschaden, in germ– is not easy because the symptoms of the decline were different from the symptoms of the damages caused by natural (biotic and abiotic) and anthropic causes.

Under the umbrella of ICP Forest Programme, were developed and implemented an European network of plots for the assessment of the parameters of the trees crowns condition known as Level I plots. The grid of the European Level I plots were established at 16 * 16 km, arranged on a transnational unified grid over Europe. In comparison with the national grids used by each country the obtained data were relevant for the evaluation of the forest health state at European level.

After 1996 were put in function the Level II monitoring plots used for the intensive monitoring and collection of comparable data related to the changes in forest ecosystems which are directly connected to specific environment at factors such as atmosphere pollution and acid deposition. Such data can help in a better understanding at the relation causes and effects in the forests decline.

Fig. 10. General aspects of silver fir crowns affected by decline in the border of the northern Carpathians (Forest District Solca)

The monitoring results contribute to the scientific basis of air pollution control policies of UN/ECE and the European Commission (EC). Fifteen years of monitoring forest condition and two decades of forest damage research have shown, however, that the discussion of recent forest damage must not be confined to the effects of air pollution alone. The comprehensive monitoring programme corresponds to the complex interrelations between natural and anthropogenic factors in forest ecosystems. Infrastructure and data of the programme are thought to be relevant for other processes of international forest policies, e.g.

those on biodiversity, climate change and sustainable forest management. In this respect the monitoring pursues the objectives of Resolution SI of the Strasbourg, Resolution HI of the Helsinki and Resolution, L2 of the Lisbon Ministerial Conference on the Protection of Forests in Europe, and contributes to global forest policies such as the United Nations Forum on Forests (ICP- Report 2007).

The monitoring results obtained each year are summarized in annual Executive Reports. The methodological background and detailed results of the individual surveys are described in Technical Reports (www.icp-forests.org).

**Methodology for the crown health condition assessment of forests**

The state of health of forest trees can be determined by assessing the foliage loss. With a little practice, this can be accurately estimated by the foresters or other trained personnel. The development of forest damage can be traced through repeated assessments of the same trees.

Loss of needles or leaves should be assessed after sprouting in spring or early summer and before broadleaves and larch display autumn coloration, at best in July and August. Evergreen conifers (fig. 11-18) may also be assessed in their winter state as long as they are free of snow. Assessments should be made under good light conditions in good weather: rain and fog render assessments inaccurate. Leaf or needle loss is estimated for the entire crown.

The crown is considered to reach from the peak of the tree to, the lowest strong green branch forming part of the crown as such; epicormic shoots on the stem are not considered, while those in the crown are.


Fig. 9.-12. Defoliation in % of Oak crowns [27].

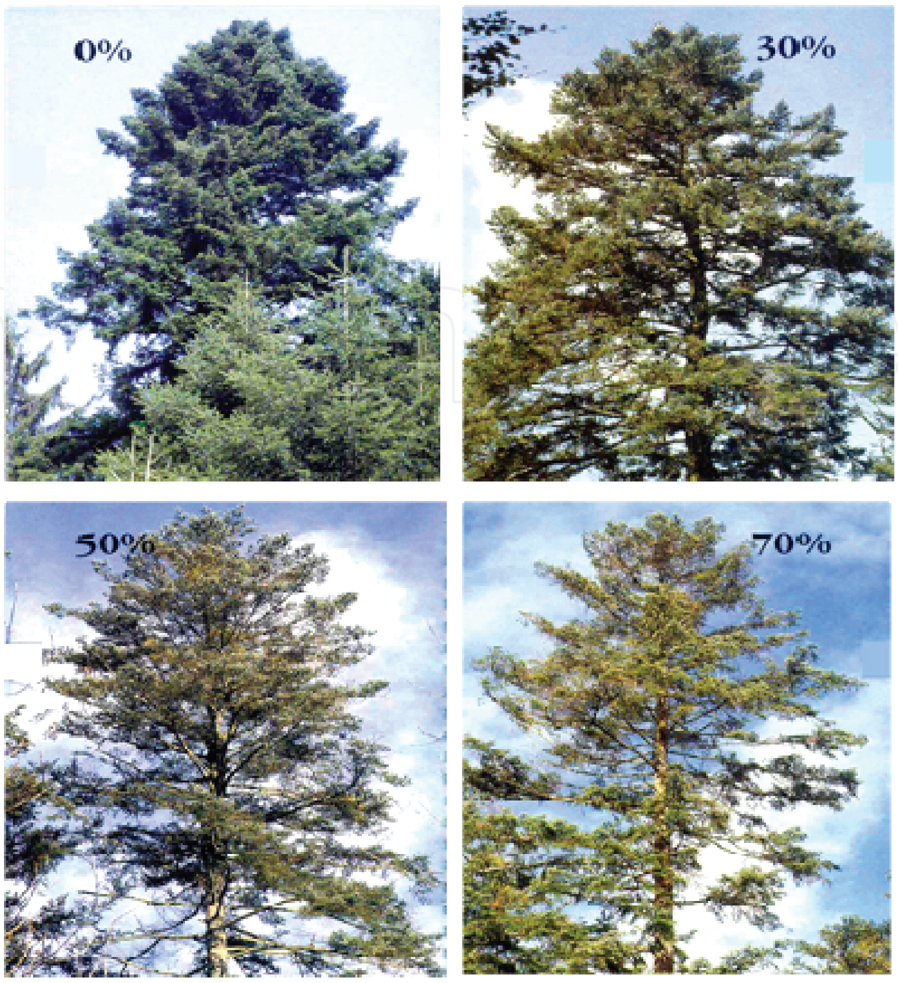


Fig. 13.-16. Defoliation in % of Beech crowns [27]

A forest tree can spread its crown to a greater or lesser extent depending on the room available within the stand. Consequently, spatial conditions must be considered in crown assessment; that is, the maximum foliage that each tree could possibly produce must be taken as a basis. The photo series (fig. 19 - 26) depicts trees of the upper storey with well developed crowns enjoying optimum light conditions. It is therefore applicable to trees of the middle and lower strata only to a limited extent. Foliage loss may be determined by comparing the tree under consideration with the corresponding photo series. The appearance of the crown is matched with one of the photos and the foliage loss estimated to a degree of 5 percent accuracy. Assessments should be made with field-glasses from a distance of at least one tree-length. Field-glasses permit precise identification of bare branches and twigs and discoloration. In subsequent surveys it is important that the tree always be observed from the same side; this should either be marked on the tree itself or noted in terms of compass direction. Leaf or needle loss due to known causes, e.g., hail, lightning, whipping, insect attack, etc., should not be included but separately inventoried [27].

## 14. Political background and objectives of ICP forests

The objectives and the strategy of ICP Forests are based on the draft long-term strategy and the work plan for the effects-oriented activities of the Working Group on Effects (WGE) of

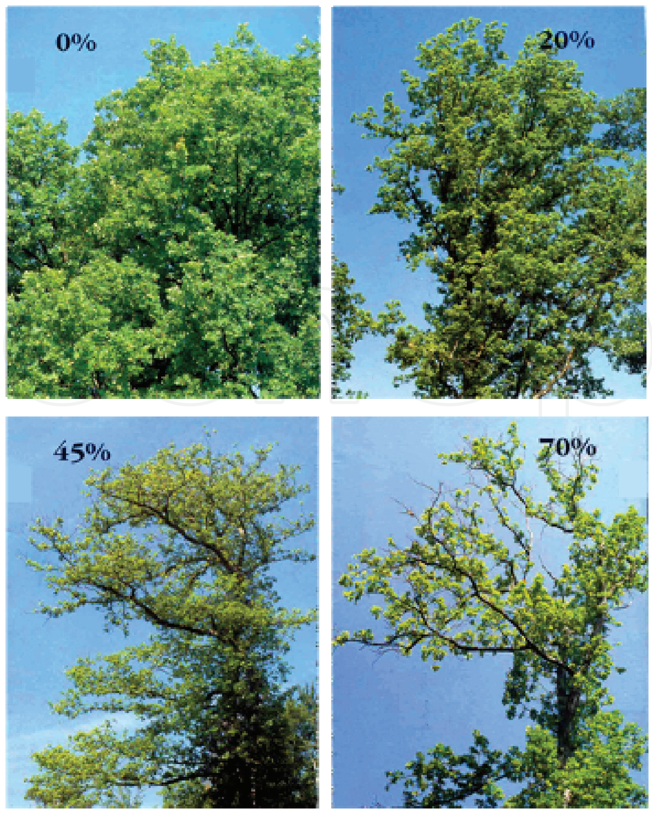


Fig. 19.-22. Defoliation in % of Oak crowns [27].

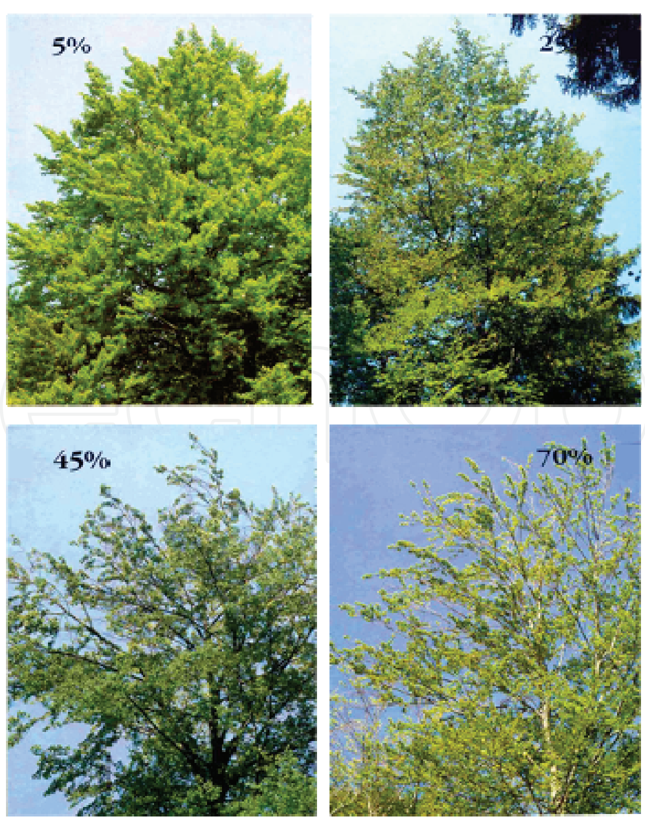


Fig. 23.-26. Defoliation in % of Beech crowns [27].

CLRTAP (Convention on Long-range Transboundary Air Pollution). The draft long-term strategy of WGE specifies the following long-term aims to which all ICP are expected to contribute:
Assessment of knowledge on

- The present status, long-term trends and dynamics, and the degree and geographical extent of the impact of air pollution, particularly, but not exclusively, its long range trans-boundary impact
- Exposure-response relationships for agreed air pollutants;
- Critical loads, levels and limits for agreed air pollutants;
- Interactive effects of air pollution and climate change on forest ecosystems
- Moreover, the long-term strategy of WGE specifies the following long-term priorities of special relevance to ICP Forests:
- Derivation of exposure-response functions for chemical and biological effects of air pollutants including investigation of nutrient nitrogen, acidifying compounds and ozone effects on ecosystem functions and on biodiversity, including combinations with other stresses (e.g. climate change and land use practices);
- Further development of models and mapping procedures, particularly for effects of nitrogen and ozone on the environment and for the description of dynamic processes of damage and recovery (acidification, eutrophication, heavy metal accumulation) by including to a larger extent biological effects;
- Evaluation of environmental benefits of air pollution control policies.
- In order to meet the information needs of the Working Group on Effects of Atmospheric Pollution (WGE), ICP Forests pursues the following two main objectives:
- Objective 1: A periodic overview on the spatial and temporal variation of forest condition in relation to anthropogenic and natural stress factors (in particular air pollution) by means of European-wide and national large-scale representative monitoring on a systematic network.
- Objective 2: A better understanding of the cause-effect relationships between the condition of forest ecosystems and anthropogenic as well as natural stress factors (in particular air pollution) by means of intensive monitoring on a number of selected permanent observation plots spread over Europe and to study the development of important forest ecosystems in Europe.

These objectives imply in accordance with the long-term priorities of WGE contributions to calculations of critical loads and levels and the assessment of their exceedances. They imply also dynamic modeling of the response of forest ecosystems to deposition scenarios expected for the future. Additional insight is gained by compiling available studies from the National Focal Centers (NFCs) and from related programmes inside and outside of Convention on Long-range Trans-boundary Air Pollution.

## 15. Strategy of ICP forests

**Monitoring activities**

In order to meet its data generation and reporting obligations, ICP Forests employs data collection at two levels.

- Large-scale monitoring (Level I) provides a periodic overview of the spatial and temporal variation in a range of attributes related to forest condition. Level I plots, national forest inventory (NFI) plots, and other related inventory plots may be combined when appropriate, feasible and necessary, according to defined and agreed procedures.

- Intensive monitoring (Level II) is carried out on plots installed in important forest ecosystems.

These plots are dedicated to in-depth investigation of the interactive effects of anthropogenic and natural stress factors on the condition of forest ecosystems.

**Quality assurance and control**

All monitoring activities are harmonized by ICP Forests among the participating countries and are laid down in this Manual. This ensures a standard approach for data collection and evaluation and can form the nucleus for a future common European forest monitoring programme. A consistent quality assurance approach is applied within the programme covering the set up of methods, data collection, submission and investigation as well as reporting. Quality assurance and control is supervised by the Programme Coordinating Group through its Quality Assurance Committee. A set of Expert Panels cares for data quality assurance within the specific surveys and for the further development of monitoring methods and standards. This includes field checks, inter-calibration courses, laboratory ring tests, and data validation.

**Data evaluation and reporting**

A range of monitoring variables is required to meet the information requirements of Convention on Long-range Trans-boundary Air Pollution and other international institutions. The Programme Coordinating Group and the Expert Panels are responsible for a data evaluation and reporting approach which takes the medium term work-plan of Working Group on Effects of Atmospheric Pollution into account. International and national data from other programmes and institutions should be included in combined analysis. The main topics for data analysis are:

- Forest condition
- Effects on forest ecosystems from
- Acidity and nitrogen
- Ozone

Contributions in the fields of

- Climate change
- Biodiversity

Trends in deposition and their interactive effects on the adaptation and vulnerability of forest ecosystems are evaluated. This includes spatial and temporal changes and cause-effect relationships with special emphasis on critical loads and their exceedances. Dynamic models and transfer functions derived from suitably selected intensive monitoring plots are used to investigate the effects of climatic factors and greenhouse gases on forest ecosystems and applied to the large scale monitoring plots. These models are validated against measured data collected at the plots. Furthermore, data gathered at the plots are used in an integrated manner to investigate the carbon sequestration potential of forests, ozone fluxes to forests and contribute to assess status and trends of forest biodiversity at the pan-European level.

**Results**

The integrative monitoring approach of ICP Forests using the Level I and Level II networks provides robust data on the health and stability of forests. This facilitates an understanding of the effects of deposition on the role and functioning of forest ecosystems in protecting soils and water. Furthermore the programme surveys can contribute to the understanding and forecast of climate change effects on forests and can be used to supply information on the sequestration of carbon and are going to provide information on forest biodiversity as an integral part of forest ecosystems. Results are published via reports and a website (www.icp-forests.org).

ICP Forests aims to provide periodic overviews on the spatial and temporal variation of forest condition in relation to man-made and natural stress factors (particularly air pollution); to contribute to a better understanding of the cause-effect relationships between the condition of forest ecosystems and man-made and natural stress factors (particularly air pollution); and to study the development of important forest ecosystems in Europe.

More specifically, to support harmonized forest monitoring by linking existing and new monitoring mechanisms at the national, regional and EU level (tab. 2); to collect quantitative and qualitative forest data related to climate change, air pollution, biodiversity, and forest condition; and to contribute information on sustainable forest management to the Ministerial Conference on the Protection of Forests in Europe.

| **Survey** | **Number of plots** | | **Assessment frequency** |
|---|---|---|---|
| | installed | Data submitted for 2007 | |
| Crown condition | 836 | 462 | Annually |
| Foliar chemistry | 904 | 200 | Every two years |
| Soil condition | 615 | 0 | Every ten years |
| Soil solution chemistry | 302 | 169 | Continuously |
| Tree growth | 811 | 70 | Every five years |
| Deposition | 657 | 353 | Continuously |
| Ambient air quality (active) | 84 | 27 | Continuously |
| Ambient air quality (passive) | 254 | 167 | Continuously |
| Ozone induced injury | 114 | 43 | Annually |
| Meteorology | 265 | 191 | Continuously |
| Phenology | 186 | 58 | Several times per year |
| Ground vegetation | 777 | 67 | Every five years |
| Litterfall | 262 | 105 | Continuously |
| Remote sensing | National data | | Preferably at plot installation |

Table 2. Surveys and number of plots for Level II monitoring. The variation in assessment frequency results in different numbers of plots with data submission for the different surveys (after www.icp-forests.org)

**Conclusions after 25 years of forest monitoring at European level**

For 25 years, forest condition has been monitored by ICP Forests in close cooperation with the European Commission. The system combines an inventory approach with intensive monitoring. It provides reliable and representative data on forest ecosystem health and vitality and helps to detect responses of forest ecosystems to the changing environment. The data collected so far provide a major input for several international programmes and initiatives, such as the Convention on Long-range Trans-boundary Air Pollution and the Ministerial Conference for the Protection of Forests in Europe.

| **Participating countries** | **Forest area (x 1000 ha)** | **% of forest area** | **Grid size (km X Uin)** | **No. of sample plots** | **No. of sample trees** | **Defoliation of all species by class (aggregates), national surveys** | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | **0** | **1** | **2 - 4** |
| Albania | 1063 | 37 | no survey in 2009 | | | | | |
| Andorra | 18 | | 16 X 16 | 3 | 73 | 60.3 | 32.9 | 6.8 |
| Austria | 3878 | 46.2 | no survey in | | | | | |
| Belarus | 7921 | 38.2 | 16 X 16 | 409 | 9620 | 27,7 | 63.9 | 8.4 |
| Belgium | 700 | 23.1 | 42/82 | 122 | 2858 | 30,7 | 49.1 | 20.2 |
| Bulgaria | 3699 | 33.3 | 42/82/162 | 159 | 5560 | 29,6 | 49.3 | 21.1 |
| Croatia | 2061 | 36.5 | 16 X 16 | 83 | 1991 | 37.2 | 36.5 | 26.3 |
| Cyprus | 298 | 32.2 | 16 X 16 | 15 | 362 | 3,0 | 60.8 | 36.2 |
| Czech Republic | 2647 | 33.6 | 82/162 | 133 | 5284 | 11.7 | 31.5 | 56.8 |
| Denmark | 527 | 12.2 | 72/162 | 16 | 384 | 69,0 | 25.5 | 5.5 |
| Estonia | 2213 | 49.1 | 16 X 16 | 92 | 2202 | 44.3 | 48.5 | 7.2 |
| Finland | 20150 | 66.3 | 162* 24 X 32 | 886 | 7182 | 58,2 | 32.7 | 9.1 |
| France | 15840 | 28.9 | 16 X 16 | 500 | 9949 | 28.7 | 37.8 | 33.5 |
| Germany | 11076 | 31 | 162*42 | 424 | 10376 | 36,4 | 37.1 | 26.5 |
| Greece | 2034 | 19.5 | | 89 | 2098 | 42.2 | 33.5 | 24.3 |
| Hu ngary | 1904 | 22.5 | 16 X 16 | 78 | 1872 | 54,8 | 26.8 | 18.4 |
| Ireland | 680 | 6.3 | 16x 16 | 30 | 599 | 69.9 | 17.5 | 12.5 |
| Italy | 8675 | 28,8 | 16 X 16 | 257 | 6966 | 24.5 | 39.7 | 35.8 |
| Latvia | 3162 | 49 | 8x8 | 340 | 8036 | 17 | 69.2 | 13.8 |
| Liechtenstein | 8 | 50 | no survey in 2009 | | | | | |
| Lithuania | 2150 | 32.9 | 8X8 / 16X16 | 983 | 5961 | 18.6 | 63.7 | 17.7 |
| Luxembourg | 89 | 34.4 | | | no survey in | 2009 | | |
| FYR of Macedonia | | | | | no survey in | 2009 | | |
| Rep. of Moldova | 318 | 9.4 | 2x2 | 622 | 13676 | 43.1 | 31.7 | 25.2 |
| The Netherlands | 334 | 9.6 | | | no survey in | 2009 | | |
| Norway | 12000 | 37.1 | 32/ 92 | 1622 | 9332 | 43.1 | 35.8 | 21 |
| Poland | 9200 | 29.4 | 16 X 16 , | 1923 | 38460 | 24.1 | 58.2 | 17.7 |
| Portugal | 3234 | 36.4 | no survey in 2009 | | | | | |
| Romania | 6233 | 26.1 | 16 X 16 | 227 | 5448 | 44.1 | 37 | 18.9 |
| Russian Fed. | 809090 | 73.2 | | 365 | 11016 | 80 | 13.8 | 6.2 |
| Serbia | 2360 | | 16 X 16/4x4 | 130 | 2765 | 68.1 | 21.6 | 10.3 |
| Slovak Republic | 1961 | 40 | 16x 16" | . 108 | 4049 | 9.3 | 58.6 | 32.1 |
| Slovenia | 1099 | 54.2 | 16 X 16 | 44 | 1056 | 18.2 | 46.4 | 35.5 |
| Spain | 11588 | 30.9 | 16 X 16 | 620 | 14880 | 17.8 | 64,4 | 17,7 |
| Sweden | 28300 | 69 | Varying | 3217 | 7097 | 59,9 | 25.1 | 15,0 |
| Switzerland | 1186 | 28.7 | 16 X 16 | 48 | 1040 | 32.3 | 49.4 | 18.3 |
| Turkey | 21389 | 27.5 | 16 X 16 | 563 | 12290 | 25.1 | 56,2 | 18.7 |
| Ukraine | 9400 | 15.4 | 16 X 16 | 1483 | 34498 | 66.4 | 26.8 | 6.8 |
| United Kingdom | 2837 | 11.7 | no .survey in 2009 | | | | | |
| **Total** | **1011322** | | **Varying** | **15591** | **236980** | | | |

Table 3. Forest surveys and defoliation classes for all tree species in European countries (2009). Results of national surveys as submitted by National Focal Centres (after www.icp-forests.org)

In the early 1980s, a dramatic deterioration in forest condition was observed in Europe and this initiated the implementation of forest condition monitoring under Convention on Long-range Trans-boundary Air Pollution. Today, the monitoring results indicate that, at the large scale, forest condition has deteriorated far less severely than was feared at that time. Stress factors like insects, fungi and weather effects have been shown to affect tree health. The drought in the Mediterranean region in the mid-1990s and the extremely warm and dry summer across large parts of Europe in 2003 led to increased levels of defoliation as a natural reaction of trees to this type of stress. The programme has also reported on acidifying deposition which is regionally correlated with defoliation and on atmospheric inputs that are accentuating other stress factors. In the past three years there has been little change in the mean levels of defoliation for the main European tree species. However, long-term trends show more deterioration than improvement (tab. 3).
The health status of forest trees in Europe is monitored over large areas by surveys of tree crown condition. Trees that are fully foliated are regarded as healthy. The Ministerial Conference on the Protection of Forests in Europe uses defoliation as one of four indicators for forest health and vitality.

- In 2009, crown condition data were submitted for 7193 plots in 30 countries. In total, 136 778 trees were assessed. This constitutes the programmer's largest number of plots for which annual data were submitted.
- In 2009, 20.2 % of all trees assessed had a needle or leaf loss of more than 25 % and were thus classified as either damaged or dead (fig. 27). This represents no change relative to 2008.
- Of the main tree species, European and sessile oak had the highest levels of damaged and dead trees, at 31.8 %.
- There were no significant changes in crown condition over the past ten years on two-thirds of the plots, but deterioration prevailed on the remaining third.
- In 2009, a fifth of the 136 778 trees studied were considered damaged or dead
- Trends vary between species, with European and sessile oak the most frequently damaged species. However, both have shown some recovery over the past five years. The health of Norway spruce and Scots pine has improved over the past 18 years. Defoliation in common beech, Holm oak and maritime pine has increased.
- There has been no significant change in tree health on most plots monitored over the past ten years. Defoliation increased on 24.4 % of plots monitored and decreased, indicating an improvement in crown condition, on only 14.9 % (fig. 28).
- Over the past 18 years there has been a clear improvement in crown condition for Scots pine and a slight improvement for Norway spruce. European and sessile oak have shown the highest mean defoliation over the past decade.
- Defoliation peaked after the extremely dry and warm summer in 2003 and has been slowly recovering since 2007. Defoliation of common beech peaked in 2004, while Holm oak showed a sharp deterioration in crown condition in the mid-1990s and again in 2005. Unfavorable weather conditions are thought to be responsible for these trends. There was a reasonably consistent increase in defoliation of maritime pine up to 2005, followed by a short period of recovery after which crown condition again deteriorated in 2009 [28], [29], [30].

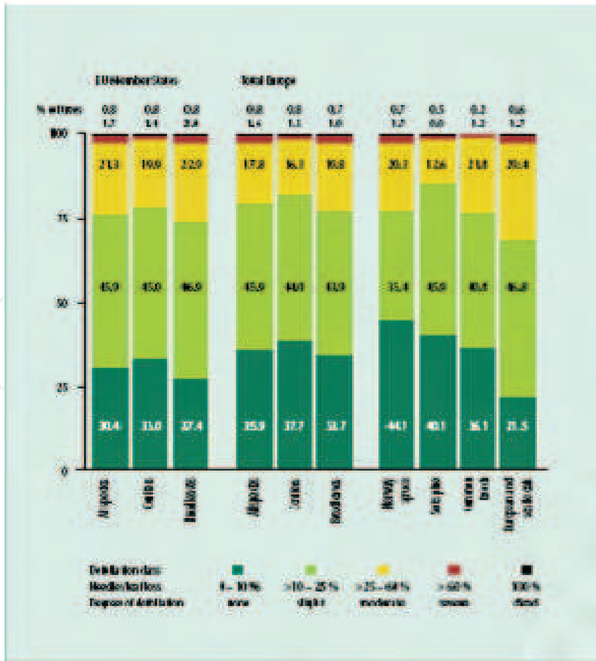

Fig. 27. Extent of defoliation for the main European tree species. Total Europe and EU, 2009. (after www.icpforests.org)

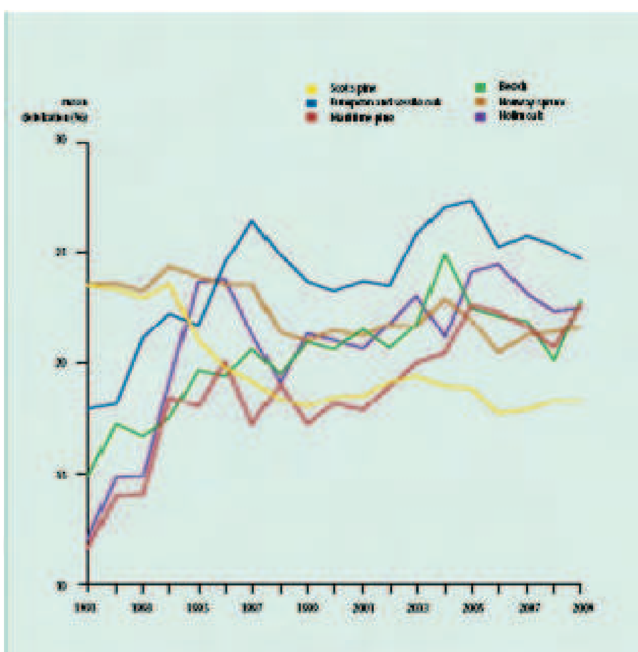

Fig. 28. Mean percentage defoliation for the most frequent tree species in European forests (after www.icpforests.org)

- Defoliation is an indicator of tree health and vitality that can be easily monitored over large areas and which reacts to many different factors, including climatic conditions and weather extremes as well as insect and fungal infestations.
- Defoliation represents a valuable early warning system for the response of the forest ecosystems to change – this is particularly relevant as climatic extremes are predicted to occur more frequently in the relatively near future.

- Deposition of pollutants from the air can affect soil and site conditions and thus the condition of forest trees.
- The status and trends in forest condition vary regionally and for different species. Local conditions may differ from the European average.

**Conclusions concerning the dynamic of atmospheric deposition**

ICP Forests began deposition measurements on intensive (Level II) monitoring plots in the latter half of the 1990s. Measurements are carried out within the forest stands (through fall deposition) and in nearby open fields (bulk deposition). In the forest canopy, some elements can be leached from the foliage and increase the measured deposition load, whereas others are taken up by leaves and needles and are so not detected in through fall. Bulk deposition is mostly lower than through fall deposition because of the additional deposition loads filtered from the air by the forest canopy. Thus, neither through fall deposition nor bulk deposition is equal to the total deposition received by the forest stands. However, through fall deposition is presented here as this reflects the inputs reaching the forest floor and so these measurements are of greater ecological relevance to forest ecosystems than open field measurements. On the plots, samples are collected weekly, fortnightly or monthly and are analyzed by national experts.

After intensive quality checks, annual mean deposition for the years 1998 to 2007 was calculated for plots with complete data sets. Slopes of plot wise linear regressions of deposition over time were tested for significance. Plot-specific means were calculated for the period 2005 to 2007.

The most relevant trends cam is formulated as follows:

- Mean annual sulphur inputs decreased by 30 % between 1998 and 2007, with significant reductions measured on half of the plots. These findings are based on deposition measurements made under the forest canopy on 157 plots located mostly in central Europe. Mean nitrogen inputs showed little change or only a very small decrease.
- The downward trend in sulphur deposition reflects the success of the clean air policies under the UNECE and the EU for sulphur emissions. In contrast, the nitrogen deposition data indicate a clear need for further reductions in nitrogen emissions.
- Deposition is generally higher on central European plots than on plots in northern and southern Europe.
- On average, through fall deposition in forests is higher than deposition on open field sites because trees filter dust and other dry deposition from the air which is then washed from the foliage to the forest floor by rain. Between 1998 and 2007, sulphate deposition on the open field sites fell by 26 %; from 6.1 to 4.5 kg per hectare per year.
- The decrease in sulphate through fall deposition (measured below the forest canopy) was higher at 34 %; from 10.0 to 6.6 kg per hectare per year (fig. 29).
- About half the plots showed a significant reduction in sulphur inputs over the 10-year study period. The data are mean values from around 150 measurement stations located mainly in central Europe.
- Mean nitrogen deposition within the forest stands fluctuated (for nitrogen measured as nitrate and ammonium) and few plots showed significant changes in through fall deposition.
- Slight decreases in mean nitrogen deposition at the open field plots were observed (fig. 30). The deposition data show the success of the clean air policies in Europe for sulphur emissions, and show the need for further reductions in nitrogen emissions [31], [32], [33].

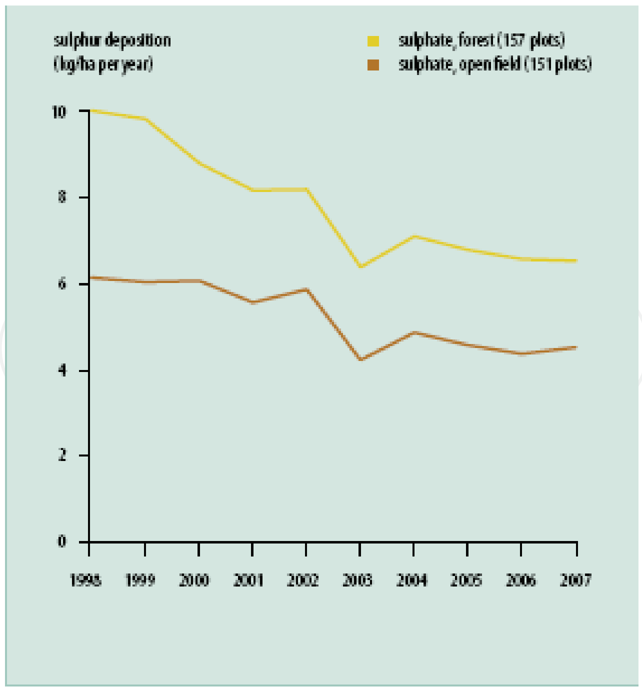


Fig. 29. Development of mean deposition of sulphate from 1998 to 2007. The forest canopy alters pollutants from the air. Inputs within the forest stands are higher than in the open field. In 2003 there was less precipitation and thus less deposition. (after ww.icpforests.org)

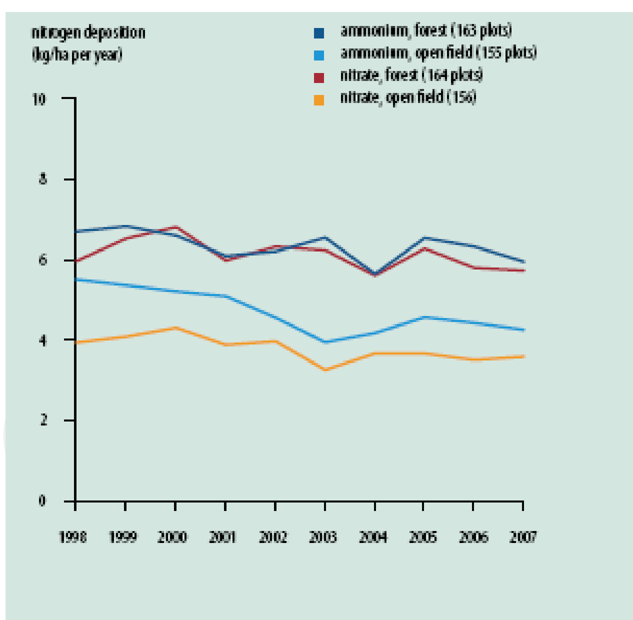


Fig. 30. Development of mean plot deposition of nitrogen compounds plots) from 1998 to 2007. Some reduction are visible in open field measurements. There was little change in deposition for the forest stands over the10 years of observation. (after www.icpforests.org)

Atmospheric deposition has been the specific focus of the programme since its inception. Current evaluations show decreasing sulphur inputs on about 50% of around 150 intensive monitoring plots since 1998, which is a result of clean air policies under the LRTAP

Convention and EU legislation. However, critical limits in the soil water are still substantially exceeded on a quarter of the plots and indicate a potential threat to forest vegetation. Earlier studies conducted under the programme have shown that the risk of storm damage is higher on acidic soils. Nitrogen inputs have hardly changed over the past ten years and the data sets now show shifts in the composition of forest ground vegetation towards more nitrogen tolerant species. Atmospheric deposition is a driver for these changes in biodiversity. Another effect of nitrogen deposition is increased tree growth which was found on intensive monitoring plots across Europe [34].

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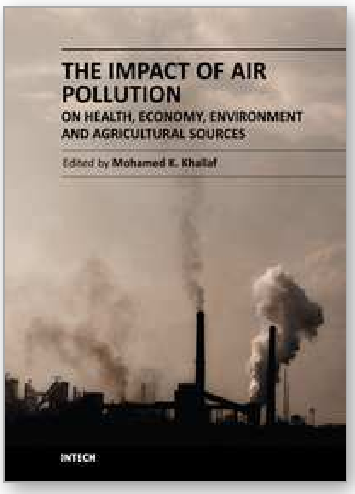


**The Impact of Air Pollution on Health, Economy, Environment and Agricultural Sources**
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This book aims to strengthen the knowledge base dealing with Air Pollution. The book consists of 21 chapters dealing with Air Pollution and its effects in the fields of Health, Environment, Economy and Agricultural Sources. It is divided into four sections. The first one deals with effect of air pollution on health and human body organs. The second section includes the Impact of air pollution on plants and agricultural sources and methods of resistance. The third section includes environmental changes, geographic and climatic conditions due to air pollution. The fourth section includes case studies concerning of the impact of air pollution in the economy and development goals, such as, indoor air pollution in México, indoor air pollution and millennium development goals in Bangladesh, epidemiologic and economic impact of natural gas on indoor air pollution in Colombia and economic growth and air pollution in Iran during development programs. In this book the authors explain the definition of air pollution, the most important pollutants and their different sources and effects on humans and various fields of life. The authors offer different solutions to the problems resulting from air pollution.

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