Parent document

Air Pollution in Mexico City:

Project-Study paper, University of Salzburg, Austria (Dr. W. Hofmann)
Department of Biophysics and in Cooperation with the
Afro-Asian Institute (Salzburg, Austria) and
International Laboratory for Air Quality and Health at QUT (Australia)

Authors: **Maricela Yip** and **Pierre Madl**

14th Dec. 2000
updates: 23rd May 2001 / 16th April 2002

Table of Contents:

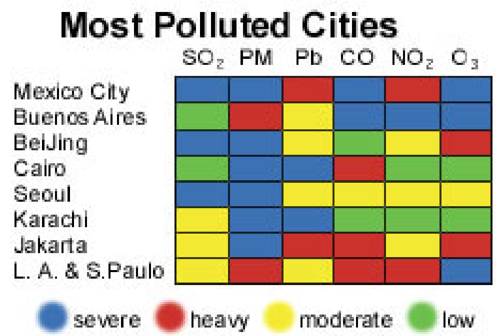

Fig.1.1: The most polluted Megacities in the world

1. Introduction- picture galery

Mexico City's air has gone from among the world's cleanest to among the dirtiest in the span of a generation. Novelist *Carlos Fuentes* first novel took place here in 1959 and was entitled "Where the air is clear" - a title he has said is ironic considering the city's now –soupy environment.

The average visibility of some 100 km in 1940s is down to about 1.5 km. Snow-capped volcanoes (*Popocatepetl*, *Ixtacihuatl*, and *Paricutin*) that were once parts of the landscape are now visible only rarely (fig.1.2). And levels of almost any pollutant like nitrogen dioxide (NO_2) now regularly break international standards by two to three times. Levels of ozone (O_3), a pollutant that protects us from solar radiation in the upper atmosphere but is dangerous to breathe, are twice as high here as the maximum allowed limit for one hour a year and this occurs several hours per day every day (fig.1.1).

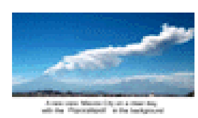

Fig.1.2: Mexico City on a clear day (50kB)

Facts and figures of Mexico city:
The Mexican Republic is formed by 31 states and the Federal District (fig.1.3). Among the states of this country there is one called the State of Mexico, which is situated in the center of the country surrounding the Federal District. The Federal District (DF) and some counties of the State of Mexico form the Mexico City Metropolitan Area (ZMCM). The Federal District is divided into 16 counties called *Delegaciones*, all of them constitute the ZMCM. From the total of 121 counties for all of Mexico, only 16 of them are considered part of the ZMCM (fig.1.4)

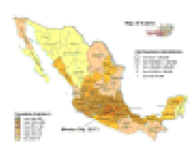

Fig.1.3: Republic of Mexico (100kB)

Federal District (Delegaciones)	**State of Mexico** (Counties)
1) Alvaro Obregón	17) Atizapan de Zaragoza

2) Azcapotzalco
3) Benito Juárez
4) Coyoacán
5) Cuajimalpa
6) Cuauhtémoc
7) Gustavo A. Madero
8) Iztacalco
9) Iztapalapa
10) Magdalena Contreras
11) Miguel Hidalgo
12) Milpa Alta
13) Tláhuac
14) Tlalpan
15) Venustiano Carranza
16) Xochimilco

18) Coacalco
19) Cuautitlán
20) Cuautitlán Izcalli
21) Chalco
22) Chicoloapan
23) Chimalhuacan
24) Ecatepec
25) Huixquilucan
26) Ixtapaluca
27) La Paz
28) Naucalpan de Juárez
29) Netzahualcoyotl
30) Nicolás Bravo
31) Tecamac
32) Tlalnepantla
33) Tultitlán

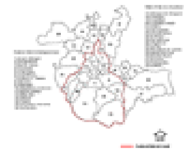
Fig. 1.4: Mexico City's Metropolitan Area (100kB)

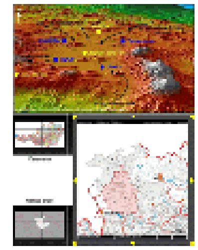
Fig. 1.5: Mexico City's altoplano / D.F. vs. Austria (380kB)

Land Use within the area of Mexico City is greatly distorted; the charts below indicate some mismanaged concept implemented by the district government. The following graphics show the distribution of land uses (fig.1.6):

Industry: In 1987 major industrial activity was carried out in the northern part of the Federal District, in *Azcapotzalco* (27% of the total), followed by *Iztapalapa* (16%), *G.A.Madero* (14%) and *M.Hidalgo* (12%), respectively. The remaining facilities are spread throughout the other districts.
Residential Distribution. Major concentrations of habitation in 1987 were *Iztapalapa* with 16.36% of the total, followed by *G.A.Madero* (12%), *A.Obregòn* (10%) and *Tlalpan* (10%). The remaining facilities are spread throughout the other districts.
Green Areas Distribution: The Federal District is poor in green areas (i.e. parks etc.); most of them are located in the south part of the city. *M.Alta* delegation represents 32% of the total with around 28,000 square kilometers followed by *Tlalpan* (30%) and *Xochimilco* (12%). The remaining areas are spread throughout the other districts.

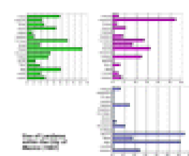
Fig. 1.6: Land-use withing the Metropolitan Area (100kB)

Mexico City is one of the worlds largest metropolitan areas, housing nearly 21 million inhabitants within the Valle de Mexico (also referred to as the Mexico City basin - see fig.1.5). The Valle de Mexico occupies ~1300km^2 at a nominal elevation of 2240 m above mean sea level, and is bordered on the east and west by mountains that rise 1000 m above the valley floor, with low points to the north and south.
The Metropolitan Area of Mexico City, also called *Zona Metropolitana de la Ciudad de México* (ZMCM), lies in a high altitude basin almost completely surrounded by hills, mountains (including dormant/active volcanoes - seismic activity is frequent and the area which is well known as an "*earthquake zone*" but with an opening to the north that extends over 4 km^2 and it is located 19°3' north latitude and 99°1' west longitude.
More than 20% of Mexico s entire population lives in the Valle de Mexico, and more than 30% of the country's industrial output is produced within its environs. Though already one of the world s largest cities, the Mexico City metropolitan area is still growing at a rate exceeding 3% annually. More than three million vehicles travel on its streets daily.

The average altitude of Mexico City is 2,240 m above sea level. At these altitudes, the average atmospheric pressure is roughly 25% lower than at sea level (fig.1.7):

$$p_{MEX} = p_{SL} \cdot e^{-h/d}$$

p_{SL}, atmospheric pressure at sea level, 1013 [mb]
h, height [m]
d, conversion constant [1/m], d = 7934.8[1/m]

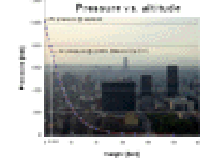
Fig.1.7: Partial pressure of Oxygen (50kB)

According to the formula given above, the atmospheric pressure in Mexico City is 764 mb. Keeping in mind that oxygen makes up 21% of the atmospheric constituents, the partial pressure of oxygen (O_2) in 2240 m altitude is roughly 160 mb, compared to the 213 mb at sea level.

This lowered partial pressure (pO_2) does have significant effects. For example, people breathing at these altitudes require more red blood cells and their blood viscosity changes significantly. Because less oxygen is available, combustion processes likewise cannot take place adequately. Such rich mixtures, on the one side, reduce the emission of nitrogen oxides, but on the other side, it enhances the emission of carbon monoxide (CO), hydrocarbons, and volatile organic compounds (VOC). Changes in engine design, the addition of catalytic converters or after burners and careful tuning considerably would reduce the major pollutants in exhaust gases. The difficulty with these approaches is that they often work well on a test bed with warm engines under suitable operating conditions, but are not so effective in poorly maintained vehicles operating under stop-start city cycles (fig.1.8; refer also to the chemistry of atmospheric pollutants, further below).
Under these aspects, this environment of about 21 mio inhabitants, most of them younger than 25 years of age, crowd together to produce not only one of the most densely populated cities but also one of the most severe air pollution scenarios on earth.

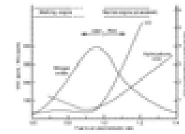

Fig.1.8: Concentration of pollutants in automobile exhaust as a function of the fuel to air ratio (ppht = parts per $100E^3$ - 50kB)

2a. Climatic Parameters - Global Factors

The climatic conditions of the state of Mexico are quite diverse; they range from a semiarid belt in the far North to a rather tropical environment in the South. Although its elevation is high, Mexico City's location at 19° north latitude provides it with a temperate climate throughout the year. The climate is generally dry, but thunderstorms are frequent and intense from June through October. Winters are slightly cooler than summers and have a more semiarid character - **see table**.

The global wind-distribution charts reveal the general trends among the most distinct seasons (January and July average - see fig.2.1).
During the ***winter*** months a very persistent high pressure system resides over the south-eastern Pacific of the northern hemisphere. This enables a weak flow of moderately tempered air (synoptic flow from the south) into the highlands of Mexico. The geographical conditions of Mexico City with its northern opening traps the air that are pushed by turbulent flow (as a result of the synoptic flow) from the north towards the southerly located mountain chain favoring an inversion zone. As mentioned previously, the location of heavy industry at the northern outskirts of the City keeps pushing their exhaust gases into the metropolitan area, which further aggravates the already tense situation present due to exhaust emissions of the automotive fleet.
The ***summer*** months, experience a stronger synoptic flow from the south, intensive sunshine, and the absence of inversed atmospheric strata by lifting the trapped masses of air and thereby cleansing the daily accumulating toxic cocktail. And still, often the winds crossing the southern mountain chain run over the cushion of firmly residing air in the valley. Like in winter, the resulting vortex further below the mountain chain pushes the air back from the northern end into the valley towards the south. The only easing effect during the summer months are the wash-out effects due to rain and lifting of the air strata during intense sunshine.

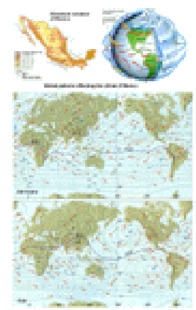

Fig.2.1: The Horseshoe latitudes are dominated by high-pressure systems (320kB)

2b. Climatic Parameters - Local Factors

Pollution levels of Mexico City are regularly above air quality standards. Up to date, fossil fuels are the primary energy source for the Mexico's industry and technology based society. Yet their combustion, especially in automobiles, release incompletely burned chemicals and oxidized species known as ***primary*** *pollutants* into the atmosphere. The dangers they pose range from eye and throat irritation to global warming. Many of the primary pollutants undergo further reaction under the influence of sunlight. The products of these photochemical reactions are called ***secondary*** *pollutants*. Primary and secondary pollutants, along with *aerosols*, which are suspended fine particles such as water droplets, dust, and soot, contribute to the brown haze observable as smog (fig.2.2).

The most important air pollutant of Mexico City are ozone (O_3), sulfur dioxide (SO_2), precursors like nitrogen oxides (NO_X), hydrocarbons (HC), and carbon monoxide (CO), that originate from the incomplete combustion of fossil fuels. At these altitudes, the partial pressure of oxygen (pO_2) is far lower than at sea level, thus combustion is far from ideal.

Most of the energy consumed in this city is related to urban transportation. A very important source of air pollution is gas exhaust from private vehicles.
The image on the right shows drastically how the prevailing atmospheric conditions affect Mexico City. A change in the temperature stratification within higher altitudes of the atmosphere hinders exhaust gases to escape the valley. Such situations and the massive generation of toxic gases can alter the trapped air into a harmful cocktail (fig.2.2).

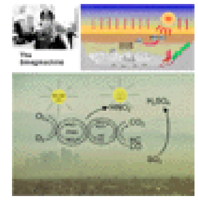

Fig.2.2: The smog machine (150kB)

As can be seen in the Conceptual Diagram illustrating important meteorological processes contributing to pollutant transport within the Mexico City Basin during a 1997 Field Campaign (Feb-March by Edgerton et al.), a distinct daily rhythm does prevail within the basin. Under certain conditions, the contribution of emissions from the previous day can accumulate with those of the present day. This inhomogeneous pollutant concentration within Mexico City is primarily based on the atmospheric system present over the basin. These circulations are highly complex.
Because of the topographic setting of the city, the moderately strong insulation associated with its tropical latitude and high elevation, and weak prevailing synoptic winds during the winter months, Mexico City is strongly affected by thermally and topographically induced circulation patterns. Three daytime flow patterns are observed during that period; a regional plain-to-plateau flow of air from the lower lying areas to the north and east into the basin from the north in the late afternoon, driven by the heating of the elevated terrain in central Mexico; local valley-to-basin flow in which southerly winds would develop and propagate through the gap in the mountains to the southeast and over the ridge forming the southern boundary of the Mexico City basin; and local upslope flows driven by the heating of the sidewalls of the mountains.

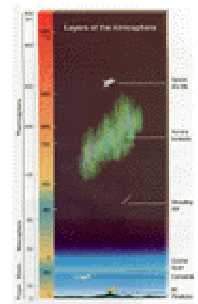

Fig.2.3: The Atmosphere (40kB)

Early Morning: The constant synoptic flow (main flow sheath of tropospherical air) has an impact on the local and regional thermally-driven flows in the area. The cooled masses of air sink along the slopes of the mountain chains and slide underneath the cold and pollutant loaded blanket of air covering Mexico City (classical inversion layer).
Noon: As the sun rises on the horizon, the vertical and horizontal advection (diverging flow) gradually shifts to a circular diffusion pattern as the cold-air pool gradually rises with the energetic solar input. The rise of the now mixed layer sucks fresh air from the northern end - by now opened up as the mixed layer rises beyond the threshold of the plateau-basin mountains (fig.2.4).
Late Afternoon: As the masses of air rise further, eventually reaching out beyond the peaks of the surrounding mountains, the synoptic flow of the upper troposphere is capable of sweeping out the masses of air. This happens as the heated vertical diffusion accelerates its circulation pattern; therefore, sucking the pollutant loaded trapped bottom air up into the higher altitudes of the troposphere (fig.2.3).

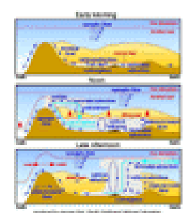

Fig.2.4: Air circulation diagram (120kB)

Unfortunately, many times of the year inversion situations like that described in the case picture of early morning persist for the entire day, thus preventing any exchange of air.

3. Air Pollution in Mexico City - Sources and Effects

Before going deeper into Mexico City's pollution problem, it is worth considering the great smog of London in 1952/53 and the resulting effects on its population. In December of 1952, London experienced an unusually cold winter conditions. In response, the people of London burnt large quantities of coal in their grates. Smoke was pouring from the chimneys of their houses and becoming trapped beneath the inversion of an anticyclone that had developed over the southern parts of the British Isles during the first week of December (fig.3.1).

Trapped, too, beneath this inversion were particles and gases emitted from factory chimneys in the London area, along with pollution, which the winds from the east had brought from industrial areas on the Continent. The total number of deaths in Greater London in the week ending the 6th December of 1952 was 2,062, which was close to normal for the time of year. The following week, the number was 4,703. The death rate peaked at 900 per day on the 8th and 9th and remained above average until just before Christmas. Mortality from bronchitis and pneumonia increased more than sevenfold as a result of the fog. It should not, however, be complacent. The air of Mexico City contains other types of pollutants, mostly of vehicle exhausts. Among these pollutants are carbon monoxide, nitrogen dioxide, ozone, benzenes and aldehydes. They are less visible than the pollutants of yesteryear but are more or less toxic, causing eye irritation, asthma and bronchial complaints.

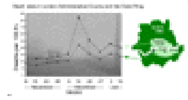

Fig.3.1: History - London and the great smog of 1952 (55kB)

Effects of Pollutant on the Urban Population: According to the nature of the pollutant, concentration levels and the period of exposure, the effects of pollution can range from a little irritation to acute sickness or even to premature death. To evaluate the effects of pollutants, two approaches are used:

i) **Toxicological** experimental studies relying mostly on animal tests and involve only few human probands.
i) **Epidemiological** studies, based on the measurable effects on the health of people when naturally exposed to a particular pollutant. The exposure time for human experiments is usually limited because of possible damage to health. Epidemiological studies can help to evaluate chronic, long-term effects.

Many compounds have been identified in polluted urban air, but their interaction, for example, sooth chemistry, is extremely complex. Photochemical pollution is now more common than was originally thought. It occurs so widely that is important to discuss it in some detail later on.

Nitrogen present in the air and as an impurity in fuels convert to nitric oxide in exhaust gases. In similar way, other trace impurities can give rise to a variety of pollutant gasses in emission. The presence of chlorine and sulfur in fuels results in the emission of gaseous chlorine and sulfur compounds.

Emission Inventory of **ozone precursors** in the ZMCM (Percentage in Pollutant Weight, 1995). The emission inventory is the basic instrument of diagnosis and planning, and offers a rational basis for decision-making. From the ZMCM emission inventory, motor vehicles make the greatest contribution to the emission of ozone precursors (55% HC and 71% NO_X), followed by thermo-electric power plants (15% NO_X), services (38% HC), industry (10% NO_X and 3% HC), and the rest from other human activities and natural sources (fig.3.2).

Although pollutant emissions have been reduced in the Mexico City metropolitan area (ZMCM), approximately 4 million tons per year are emitted at the present time (data of 1998). According to local census data, the main source of most pollutants is the internal combustion engine (75%), followed by natural sources (12%), services (10%) and industries (3%). Sulfur dioxide is related to industrial activity, while carbon monoxide, nitrogen dioxide and hydrocarbons arise mainly from transport emissions.
The main sources of **sulfur dioxide** (SO_2) are industries (57%), followed by internal combustion engines (27%) and services (16%).
Some **particles** emissions in the city are due to natural sources (erosion).

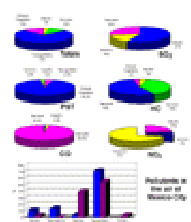

Fig.3.2: Main Pollutants in D.F.

- **Sulfur dioxide** (SO_2): Sulfur dioxide can also be oxidised under photochemical conditions but the sulfur-oxygen bond is very strong so that sulphur dioxide cannot undergo the photo-dissociation. The oxidation process involves the hydroxyl radical and in combination with humid air (water aerosols) it reacts to sulfuric acid (H_2SO_3, H_2SO_4), that, if inhaled, exerts corrosive properties to the nasal mucus, the trachea of the lungs and the alveolar tissue (fig.3.3). Ultimately resulting in respiratory problems and severe attacks of coughing - **see table**.

$$OH\cdot + SO_2 \rightarrow HSO_3$$
$$HSO_3 + O_2 \rightarrow HSO_5 \rightarrow HO_2 + SO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$

Fig.3.3: Effects of SO_2 (60kB)

- **Ozone** (O_3) is a colorless gas produced in the presence of ultraviolet light. It is a chemically unstable gas that will enter oxidation reactions with other materials faster than normal oxygen (O_2). The buildup of substantial concentrations of Ozone is a major atmospheric pollution problem in the ZMCM. The Mexican ozone standard of

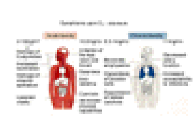

Fig.3.4: Effects of O_3

0.11ppm is frequently exceeded, so the reduction of this pollutant has been taken as an important indicator of improvement in air quality (fig.3.4).

(80kB)

- **Main sources**: Atmospheric reactions of hydrocarbons (emitted from the internal combustion engine) and nitrogen oxides under the influence of ultraviolet in sunlight.
- **Main effects**: It affects the growth of trees and plants in general. Specific effects of this pollutant on human health have also been detected in the form of irritated eyes, persistent headaches, and increased hyper-reactivity.

  With the increase of traffic, the associated pollution impact in cities and the realization that ozone is a toxic substance, authorities moved away from attributing ozone a beneficial effect to an attitude that regards it as a potential hazardous substance for the respiratory system.

In the spring of 1995, a long-term study of US researchers created widespread attention. In this study mice were exposed to high concentration of ozone gas; in turn these mice developed lung cancer (the selected concentrations were 1000 to 2000mg/m^3, well beyond any observed levels; furthermore, a very sensitive strain of mice was selected. With the usually concentration of 240 mg/m^3 neither rats nor mice showed a significantly increased cancer risk). The carcinogenic effect of ozone in air is thus still disputed. Regarding the non-carcinogenic, harmful effects of increase ozone levels, the following observations were made - **see table**.

In reference, the Ozone Protection Act for European countries (e.g. in Austria it went into effect on May 1st of 1992), group ozone concentration into three categories - according to the average mean of 3-hours - **see table**.

- **Nitrogen Oxides (NO_x)**: NO_X and HC's are precursors of photochemical smog. In the formation process, part of NO_X is divided to produce an atom of oxygen, which reacts to form ozone (O_3) at ground level (fig.3.5).
  The oxides of nitrogen are mainly formed in combustion chambers (such as in car engines) when the nitrogen in air is heated above 1370°C. To reduce NO_X emissions, combustion temperature have to be reduced, burning time shortened, or nitrogen concentration decreased. Specific effects of this pollutant on human health have also been detected - **see table**.

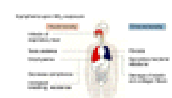
Fig.3.5: Effects of NO_X (50kB)

Synergistic effects of nitric oxides with primary and secondary pollutants:

In the atmosphere, nitric oxide is oxidized to nitrogen dioxide, which is a major constituent of smog:

$$N_2 + O_2 \rightarrow 2NO$$
(w/n the combustion engine)

Smog appears brown partly because it absorbs sunlight at wavelengths less than 400 nm. Light of these wavelengths dissociates nitrogen dioxide into nitrogen oxide (NO) molecules and oxygen (O) atoms:
Light with a wavelength of 400 nm is at the violet end of the visible spectrum; so when it is absorbed, the remaining transmitted light appears yellow-orange (fig3.6).

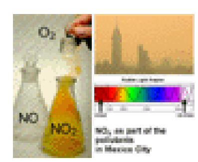

Fig.3.6: $2NO + O_2 \rightarrow 2NO_2$ (90kB)

The gas NO is colorless. When it is exposed to air, it is rapidly oxidized to brown NO_2 (fig3.6.). The oxygen atom produced by the dissociation of NO_2 is a highly reactive biradical. It is a strong oxidizing agent that can oxidize many of the primary pollutants and even reacts with O_2. The most evident product of its action are ground level based ozone (O_3) and the **p**eroxy- **a**cetyl- **n**itrates (PAN).

$$NO_2 \rightarrow h\cdot f\ (<430nm) \rightarrow NO + \cdot O\cdot$$

$$\cdot O\cdot + O_2 + M \rightarrow O_3 + M$$
(where M as a third party collision partner, e.g. N_2, able to absorb kinetic energy)

These compounds are highly toxic substances, even at concentrations of less than 0.1 ppm; and exposure to them at concentrations of 0.5 ppm for a few minutes does cause eye irritation.

$$O_3 + NO \rightarrow O_2 + NO_2$$

.... to close the loop or reacts further with HC's to ....

Many reaction paths lead to the formation of PAN. In one common path, an ·O· atom first abstracts an ·H atom from a molecule of unburned hydrocarbons in fuel (HC's - member of the VOC-family):

$$CH_4 + \cdot O\cdot \rightarrow \cdot CH_3 + \cdot OH$$

The hydroxyl radical, ·OH, is a common oxidizing agent in smog. The methyl radical, $\cdot CH_3$, is also highly reactive. Hydroxyl radicals react with many substances, including fuel molecules that were only partly oxidized in an engine; i.e. acetaldehyde, CH_3CHO (another member of the VOC-family) , reacts with the highly reactive hydroxyl radical to produce yet another radical:

$$CH_3CHO + \cdot OH \rightarrow CH_3CO\cdot + H_2O$$

The VOC-radical ($CH_3CO\cdot$) is also highly reactive and combines with molecular oxygen to form a peroxyl radical:

$$CH_3CO\cdot + O_2 \rightarrow CH_3CO\text{-}O_2\cdot$$

The peroxyl radical combines with NO_2 to form PAN

$$CH_3CO\text{-}O_2\cdot + NO_2 \rightarrow CH_3CO\text{-}O_2\text{-}NO_2$$

= PAN

Catalytic converters in automobiles help to control smog by converting the nitric oxides back to nitrogen and oxygen. They also complete the oxidation of unburned and partially burned hydrocarbons.

PAN can be considered as a severe eye irritatant. This compound is the principal member of a homologous series of similar nitrated compounds, which include higher peroxy-alkyl and some aromatic forms. Modern motor fuels have often tended to take on an increasingly aromatic character that has appeared to accompay the removal of lead in fuel. Compound such as benzene and toluene are released in large quantities by vehicles - this includes peroxy-benzoyl nitrate, abbreviated as **PBN** ($C_6H_5O_2NO_2$), which is a particularly potent eye irritant. The PAN class of compounds can often be detected in the remote atmosphere if there are large pollutant sources upwind. Although some nitrogen oxide in the polluted atmosphere will end up as PAN type compounds, other important reactions are possible (see also fig.2.2).
Although there is no air quality standard for PAN, high PAN concentrations are a good indicator of the organic oxidizing capacity of the urban air mass, since they are directly connected to organic peroxy radical formation and nitrogen dioxide (both ozone-forming precursors). During the field study mentioned above, PAN was typically 90% of the total PANs observed, with the rest of the PAN's being approximately 9% peroxy-propionyl nitrate (**PPN**), and approximately 1% peroxy-butyl nitrate (**PPB**). Maximum values for PAN, PPN, and PPB were 35, 6, and 1 ppb, respectively. These high levels of PAN's trap an appreciable amount of the nitrogen dioxide, thus slowing the reaction of OH with NO_2 to form nitric acid and subsequently ammonium nitrate aerosols (see Particular Matter - further below).

Nitric Acid (HNO_3): NO_X in combination with humid air (water aerosols) react to form nitric acid (HNO_3), that, if inhaled, exerts corrosive properties to the nasal mucus, the trachea of the lungs and the alveolar tissue. Ultimately resulting in respiratory problems and severe attacks of coughing - **see table**.

i) conversion of NO_2 via photolytic oxidation to NO_3: $NO_2 + O_3 \rightarrow NO_3 + O_2$

which will subsequently react with NO_x: $NO_3 + NO_2 \rightarrow N_2O_5$
$NO_3 + NO \rightarrow 2NO_2$

ii) reaction of nitric oxides with OH·: $NO + OH\cdot \rightarrow HNO_2$

$NO_2 + OH\cdot \rightarrow HNO_3$

iii) reaction between NO and NO_2: $NO + NO_2 + H_2O \rightarrow 2HNO_2$

$HNO_2 + h\cdot f\ (<400nm) \rightarrow NO + OH\cdot$

End products of these oxidation reactions are nitrous (HNO_2) and nitric acid (HNO_3); as these are recycled in that loop, they are considered as sources of OH radicals.

Under constant illumination, the rise in O_3 concentration shows a decreasing NO/NO_2 ratio. For this to happen there needs to be another source of oxidant, as the reaction sequence illustrated above do not result in any overall production of ozone. The production of ozone occurs through reactions in which the hydroxyl radical (OH·) plays a key role, as it attacks a variety of pollutants in the urban air:

$$OH\cdot + CH_4 \rightarrow H_2O + CH_3\cdot$$
$$OH\cdot + CH_3CHO \rightarrow H_2O + CH_3CO$$
$$OH\cdot + CO \rightarrow H + CO_2$$

As an initial simplification, methane is regarded as an alkane. The radical product of the above reaction becomes involved in subsequent reactions that oxidise NO to NO_2 and regenerate OH radicals simultaneously. Methane (CH_4) oxidation proceeds as follows:

$$CH_3\cdot + O_2 \rightarrow CH_3O_2\cdot$$
$$CH_3O_2\cdot + NO \rightarrow CH_3O\cdot + NO_2$$
$$2CH_3O\cdot + O_2 \rightarrow 2HCHO + H_2O$$
$$2CH_3O_2\cdot + O_2 \rightarrow 2HCHO + HO_2\cdot$$
$$HO_2\cdot + NO \rightarrow NO_2 + OH\cdot$$

Water (H_2O) can also react photo-chemically or with ozone, hydrogen (H) or oxygen (O) to regenerate hydroxyl radicals. Formaldehyde (HCHO) can photo-dissociate into H and formylium (HCO^+) or react with O_2 to give hydro-peroxyl radical ($HO_2\cdot$) and carbon monoxide (CO). The reactions above can be summed up to show the importance of the presence of hydrocarbons in generating nitrogen dioxide in photochemical smog:

$$CH_4 + 2O_2 + 2NO \rightarrow HCHO + H_2O + 2NO_2$$

This equation indicates that the oxidation of nitric oxide has not used ozone. Thus the presence of alkane such as methane in the polluted urban air provides a way in which nitric oxide can be oxidised without consuming ozone. The attack of the OH on acetaldehyde (CH_3CHO) yields the acetyl radical ($CH_3CO\cdot$), which oxidises along the following path, yielding the methyl radical ($CH_3\cdot$) mentioned above:

$$CH_3CO + O_2 \rightarrow CH_3COO_2$$
$$CH_3COO_2 + NO \rightarrow CH_3CO_2 + NO_2$$
$$CH_3CO_2 \rightarrow CH_3\cdot + CO_2$$

The atomic hydrogen produced in the reactions above, or from the photo-dissociation of formaldehyde can react with $HO_2\cdot$ to produce OH· that can in turn initiate further attack on organic compounds, or it can form a hydro-peroxyl radical:

$$H + O_2 + M \rightarrow HO_2\cdot + M$$

(where M as a third party collision partner, e.g. N_2, able to absorb kinetic energy)

Thus, aldehydes also provide effective ways of oxidising NO to NO_2. This nitrogen dioxide photolyses to produce further O_3 and NO for reoxidation. While there are loss processes in the cycles, the build up of ozone throughout the day can thus be explained.


Fig.3.7: Effects of VOC's (80kB)

- **Volatile Organic Compounds** (VOC): This is a group of substances that is composed of a pool of different molecules of various origins. The most commonly observed health effects are shown in fig.3.7. Referring to the field study of Edgerton et al. (1997), the highest concentrations measured during the morning hours (0700-0900 CST), and these were often 3 times the concentrations measured later in the

day (favors O_3 formation, see VOC:NO_x-ratio or fig.3.8 (further below).
Biogenic processes generate some VOCs, thus occur naturally. The majority, instead, are produced by human activity. The common VOC's are basically made of hydrocarbons and are discussed in depth in most organic chemistry book.
Nevertheless, a few things should be said about HC's - a subfamily of the VOCs:

Hydrocarbons (HC): Smog chemistry involves much more complex molecules. Although OH radicals in the atmosphere readily attack the alkanes, especially the larger ones, other classes of organic compounds are more active in urban atmospheres. It is often useful to describe organic compounds in terms of their photochemical ozone creation potential (**POCP**). The values are chiefly related to the rate of attack by OH· and then the scale set such that ethylene (C_2H_4, which is a strong ozone producer), takes the value of 100. It should be noted that accurate estimates of the POCP require more than a simple measure of the rate of OH· attack. This is because other species in the atmosphere can be involved in smog reactions that will produce or consume ozone. The potential of aromatic compounds, such as toluene and benzene, to produce smog is clear from their high POCP rating (see table on the right).
Alkanes, such as butene (C_4H_8), are attacked by ozone, atomic oxygen, or the hydroxyl radical. Ozonolysis by an attack of OH· is common in the atmosphere. A typical reaction scheme might be written as:

Photochemical ozone creation potential (POCP) for various VOCs:

Gas	POCP
Methane (CH_4)	0.7
Ethane (C_2H_6)	4.0
Ethene (C_2H_4)	100
n-butane (C_4H_{10})	41
benzene (C_6H_6)	19
toluene (C_7H_8)	56

$$OH\cdot + CH_3CH{=}CHCH_3 \rightarrow CH_3CHOHCHCH_3$$
$$O_2 + CH_3CHOHCHCH_3 \rightarrow CH_3CHOHCH(O_2)CH_3$$
$$NO + CH_3CHOHCH(O_2)CH_3 \rightarrow CH_3CHOH + CH_3CHO + NO_2$$

It shows the degradation of larger organic molecules into smaller, more oxidised ones.

The formaldehyde in the polluted atmosphere constitutes an important source of atomic hydrogen and therefore hydro-peroxyl and hydroxyl radicals:

$$HCHO + h\cdot f\ (<370nm) \rightarrow H + HCO$$
$$HCHO + h\cdot f\ (<370nm) \rightarrow H_2 + CO$$

Hydrogen peroxide (H_2O_2) may be produced through the above two reactions:

$$M + 2OH \rightarrow H_2O_2\cdot + M$$
$$2HO_2. \rightarrow H_2O_2 + O_2$$

HC's with their characteristic smell are the main components of fuels; therefore, they are usually found in low concentrations suspended in the atmosphere in any urban area (gas or liquid phase) and are often emitted when combustion is incomplete.

- Main sources: Incomplete combustion of fuels and other substances containing carbon (due to the use of aromatized fuel). Processing, distribution and use of oil compounds, such as gasoline, diesel, organic solvents, etc. Also fires, chemical reactions in the atmosphere and bacterial decomposition of organic matter in the absence of oxygen.
- Main effects: Disturbances in the respiratory system. Some hydrocarbons are potent mutagens, i.e. cause cancer. Main effect at the ZMCM is the reaction of HC and NO_x to form ozone in the presence of sunlight. Specific effects of these pollutants on human health have also been detected, when in interaction with other atmospheric chemicals.

  Ozone is best generated when the initial components of VOC and NO_X are present at a ratio of: VOC:NO_X = 8:1

$$C_2H_6 + OH \rightarrow C_2H_5\cdot + H_2O$$
$$C_2H_5\cdot + O_2 \rightarrow C_2H_5O_2\cdot$$

$$C_2H_5O_2\cdot + NO \rightarrow C_2H_5O\cdot + NO_2$$
$$NO_2 + h\cdot f\ (<430nm) \rightarrow NO + \cdot O\cdot$$
$$\cdot O\cdot + O_2 + M \rightarrow O_3 + M$$

(where M as a third party collision partner, e.g. N_2, able to absorb kinetic energy) .... for the continuation of the reaction, see above (synergistic effects of NO_x) ....

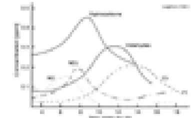
Fig.3.8: Concentration of gases in photochemical smog (50kB)

- **Carbon Monoxide**(CO): It is a colorless and odorless gas. Oxidation to carbon dioxide does occur in the atmosphere, although very slowly.
    - Main sources: Incomplete combustion of hydrocarbons and substances containing carbon. Internal combustion engines burning fossil fuels, such as gasoline and diesel. Natural sources of CO production can be detected in wild- or in campfires.
    - Main effects: Carboxi-haemoglobin is formed by the combination of carbon monoxide and haemoglobin in the blood and prevents oxygen being carried from the lungs to the target tissues (fig3.9).


Fig.3.9: Effects of CO (65kB)

Thus, it further decreases the oxygen-carrying efficiency of haemoglobin not only by the decreased altitude, but also because it occupies the binding sites of the heme-group of the red blood cells with the oxygen. It also affects the central nervous system, causing changes in pulmonary and cardiac functions, headache, fatigue, sleepiness, respiratory problems, and even death. Specific effects of this pollutant on general human health have also been detected.
Effects of Carbon-monoxide - **see table**.

- **Particle Matter** (PM) and Aerosols: A persistent haze blankets the city, especially during winter, and there is great concern among residents and visitors about the effects of suspended particles on health. Aerosols that contribute to this visibility degradation are usually a combination of primary and secondary particles. Primary particles are directly emitted from different sources (these ultrafines are found in the size range below 1µ in diameter), while secondary particles form in the atmosphere from gaseous emissions of sulfur dioxide, oxides of nitrogen, ammonia, and heavy organic gases. Secondary aerosol formation may occur under **stagnant air conditions**, after gaseous emissions from different sources have mixed and aged, and when pollutants generated on previous days accumulate or are recycled by winds and are stored overnight in surface-based inversions.
It is well known that dust and particle bound emission are causes of acute and chronic bronchio-pulmonar illnesses in the environment. They often are associated with **PAH** (poly-aromatic hydrocarbons), **PCB** (penta-chlor-phenol) and furanes / dioxins, as they readily attach on non-volatile aerosols. These particles tend to condense in the bronchio-pulmonar area where they are easily absorbed by the tissue. Furthermore, as these particles often contain heavy metals, PM represent a significant source of the toxic load taken up by humans, and are directly related to cardio-vascular diseases - **see table**. Unfortunately, current PM-detectors register only particle mass. However, studies have hown that particle number is much more relevant than their mass. Thus, standard detection equipment focuses on mass only, thereby detecting only a fraction of the particle inventory. State-of-the-Art equipment (such as ELPI and SMPS) shows that even when ultrafine numbers are high, their mass is practically zero. Hence, PM-inventories recorded by weighing machines such as TEOMs - used by governmental health authorities - go largely undetected.
Diesel fumes are especially problematic as they contain nitro-aromates; a group of chemicals that are used to accelerate the combustion process of diesel fuel. Nitro-aromatic compounds are known for their potentially mutagenic effect within the GIT(gastro-intestinal tract). Initially they cause diarrhoea (fig.3.10). Indeed, both short- as well as longterm exposure seem to affect the **Epigenome** and thus increasingly underline the relevance of aerosol inhalation and its effects on gene activity (the following review sheds some light into this issue: Health effects of Aerosol exposure - **see text**)

A part of the acid molecules produced in the reactions above - particularly HNO_2 and HNO_3 reach the surface by dry deposition owing to turbulent movements in the near surface air. Further, HNO_3 can be removed from dry air by cloud and precipitation elements (wet deposition) or it can condense to form nitrate aerosols. Since nitric acid vapour changes phase together with naturally occurring ammonia (NH_3), ammonium nitrate (NH_4NO_3) is an important compound in the range of fine particles:

$$NH_3 + HNO_3 \rightarrow NH_4NO_3 \text{ (solid)}$$

Fig.3.10: Effects of aerosols (100kB)

Ammonium nitrate forms at lower temperatures (during cold nights) and decomposes at higher temperatures (during the day). It is indicated that in summer gas phase nitrate has a greater concentration than particulate nitrate, while in winter the inverse situation can be observed.

4.a Energy Production and Consumption

Most of Mexico City's energetic requirements are met by fossil fuel derivatives; i.e. petroleum. It is a complex mixture of organic compounds, mainly hydrocarbons, with smaller quantities of other organic compounds containing nitrogen, oxygen, sulfur, and other trace elements. The usual first step in the refining or processing of petroleum is the separation of the crude oil into fractions on the basis of their boiling points (fig.4.1). Only certain fractions are taken from that mixture. The fractions that boil at higher temperatures are made up of molecules with larger numbers of carbon atoms per molecule. The fractions collected in the initial separation require further processing to yield a usable product. In the case of gasoline, modifications must be made to render it suitable for use as a fuel in automobile engines. Similarly, the fuel oil fraction may need additional processing to remove sulfur before it is suitable for use in an electrical power station or domestic heating system.

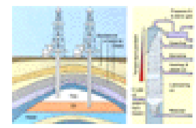

Fig.4.1: Extraction and processing of natural gas and oil (145kB)

National Oil Production: The production of national oil company PEMEX (Petróleos Mexicanos), represents the main energy production of the country and amounts to about 4.5% of total world production.
The chart (fig.4.2.) shows the rather flat (constant) rate of production over the last 20 years.
Composition of the produced oil-fractions within the fuel sector: The main commercial fuels are LPG (liquefied petroleum gas), gasoline (petrol), diesel and fuel oil (production figures for 1995, 1996 and 1997 in thousands of barrels per day, were obtained from PEMEX.
Consumed Oil Products: The volume of internal purchases of oil products and natural gas are shown in the plot. It is important to mention that oil production from sources in Mexico is not only for national consumption but a significant volume is also exported world-wide.

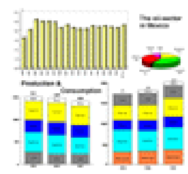

Fig.4.2: Oil production / consumption (125kB)

Distribution of Energy Consumption in Mexico (1995): The main consumers of energy produced in Mexico are transportation and industry, as showed in the following graphics; the domestic sector does contribute considerably as most electrical energy is produced by coal-combustion reactors (fig.4.3).
Type of Fuel Consumed by Sector at the ZMCM (1994): Energy consumption distribution is similar to the rest of the country, with transportation as the main energy consuming sector.

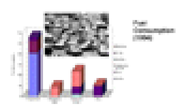

Fig.4.3: Fuel consumption (55kB)

Energetic Consumption by Type of Transportation (1989): Private vehicles accounted for 78% of energy consumption, followed by 9% on collective taxis, 7% on suburban transport, 4% on public buses, 1% on the Metro system, and finally, less than 1% on trams (fig.4.4).
Number of Vehicles in Mexico City. Being the biggest urban population center in the world, it spreads over a large area, thus has very demanding transportation requirements. 84% of its inhabitants use public transport, which accounts for 7% of the total number of vehicles on the roads. Private vehicles make up 71%.
This situation creates the following urban problems: heavy vehicle circulation in urban areas, crowds of pedestrian in the downtown area, overloaded roads, intense pollution due to fossil fuel powered and lowered efficiencies of public services.

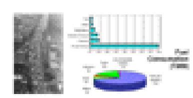

Fig.4.4: Vehicle consumption (60kB)

4.b Common Fuels

A fuel is defined as any substance, solid, liquid or gas which may be easily ignited and burned to produce heat, light or other useful forms of energy. For example, coal, charcoal, gasoline, kerosene, light oils, fuel oils, natural gas, and liquefied petroleum gases (LPG), are the most common fuels used in Mexico.
As fossil fuel products do contain the highest energetic value per volume unit, the principal fuels used in Mexico

are derived from petroleum (a mix of hydrocarbons) that undergoes refining to obtain the desired fraction (fig.4.1). fossil fuels (hydrocarbons) obtained from oil refining (fig.4.1).
Gasoline & Petrol: Petrol is a mixture of lighter (volatile) hydrocarbons, whereas gasoline contains the heavier ones. Depending on the source of the crude oil, it may contain varying amounts of cyclic alkanes and aromatic hydrocarbons in addition to alkanes. Straight-run distillate consists mainly of straight-chained hydrocarbons, which in general are not very suitable for use as fuel in an automobile engine as they burn too rapidly; i.e. the piston receives a single hard slam rather than a strong smooth push. The result is a "knocking" or pinging sound; the efficiency with which the energy of gasoline combustion is converted to power is reduced.
Thus fuel is rated according to octane number. Fuel with high octane numbers burn more slowly and smoothly, and thus are more effective fuels, especially in engines in which the gas-air mixture is highly compressed. It happens that the more highly branched alkanes have higher octane numbers than the straight-chain compounds. Because straight-run gasoline contains mostly straight-chain hydrocarbons, it has a low octane number. It is therefore subjected to a process called "cracking" to convert the straight-chain compounds into more branched molecules. Cracking is also used to convert some of the less volatile kerosene and oil fractions into compounds with lower molecular weights that are suitable for use as automobile fuel. In the cracking process, the hydrocarbons are mixed with a catalyst and heated to 400 to 500°C. The catalysts used are naturally occurring clay minerals, or synthetic Al_2O_3-SiO_2 mixtures. In addition to forming molecules more suitable for gasoline, cracking results in the formation of hydrocarbons of lower molecular weight, such as ethylene and propene (used in a variety of processes to form plastics and other chemicals).
In past decades, the octane number of a given blend of hydrocarbons was improved by adding an antiknock agent (a substance that helps control the burning rate of the gasoline). The most widely used substances for this purpose were tetraethyl lead $(CH_3CH_2)_4Pb$, and tetramethyl lead $(CH_3)_4Pb$. Such gasoline contained 0.5 or 1 mL of one of these lead compounds per liter with a resultant increase of 10 to 15 in octane rating. Because of the environmental hazards associated with lead, their use in gasoline has been drastically curtailed. This metal is highly toxic, and there is hard evidence that the lead released from automobile exhausts is a general health hazard.

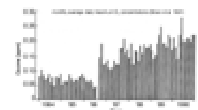
Fig.4.5: PEMEX's change from leaded to unleaded fuel and O_3 concentration in Mexico City (40kB)

Although other substances have been tried as antiknock agents in gasoline, none of these has proved to be an effective and inexpensive antiknock agent that is environmentally safe. Therefore, engine-manufacturers since 1975 were forced to redesign engines in order to make them operate with unleaded gasoline. The gasolines blended for these cars are made up of more highly branched components and more aromatic components, because these have relatively high octane ratings (increased aromaticity).
The introduction of unleaded fuels in Mexico induced more serious photochemical smog because of the enhanced degree of reactivity (aromaticity) of the emissions. This is particularly true if the change is not accompanied by the introduction of catalytic converters; for example, dramatic changes took place in Mexico City after the introduction of a new fuel in September of 1986. There was a rapid increase in ozone concentrations immediately after the fuel change (fig.4.5).

This new fuel was unleaded because of a desire to reduce the lead concentrations in the atmosphere of the city. Petróleos Mexicanos has been reluctant to release information on the formulation of its gasoline, but it has been widely assumed that the octane rating of the new unleaded fuel was maintained through the addition of more reactive hydrocarbons. In fact, the experience in Mexico City has emphasized the sensitivity of the urban photochemistry to fuel formation.

The Internal Combustion Engine:
Internal combustion engines are devices that generate work from combustion reactions. Combustion products under high pressure produce work by expansion through a turbine or piston (Carnot-cycle). The combustion reactions inside these engines are not necessarily neutralizing or complete and air pollutants are produced.
There are three major types of internal combustion engine in use today:

1. The **spark ignition engine**, which is used primarily in automobiles.
2. The **diesel engine**, which is used in large vehicles and industrial systems where cycle efficiency offers advantages over the more compact and lighter-weight spark ignition engine.
3. The **gas turbine**, which is used in aircraft due to its high power/weight ratio and is also used for stationary power generation.

Each of these types of engine is an important source of atmospheric pollutants. Automobiles are the major source of carbon monoxide, unburned hydrocarbons, and nitrogen oxides.
Diesel engines are notorious for the black smoke they can emit, and gas turbines because of soot emission.
The ideal efficiency of an ordinary automobile engine is about 56%, but in practice the actual efficiency is about 26% (fig.4.6). Engines of higher operating temperatures (compared to sink temperatures) would be more efficient,

but the melting point of the material the engines are made of suppresses the upper temperature limit at which they can operate. Higher efficiencies await engines made with new materials with higher melting points as already proved with ceramic engines.

The ideal efficiency (according to the 2nd law of thermodynamics) given in [%]:

$$\eta = 100 \cdot \frac{T_{hot} - T_{cold}}{T_{hot}}$$

T_{hot}, combustion temperature in the engine [K]
T_{cold}, exhaust gas temperature at engine [K]

As can be see in the representative image, an average car (at sea level) uses only about 26% of the provided energy, the remaining 74% are lost. However, at altitudes of 2240 m with reduced partial oxygen pressure, the combustion process is even further restricted, and along with it, resulting in a reduced energetic output of the engine; in Mexico City it can be as low as 20%!

Furthermore, the use of a built-in air-conditioner, lowered tire pressure, speeds exceeding 90 km/h, and aggressive driving pushes efficiency even further down. In Mexico City the idling and coasting losses are probably excessively elevated, as countless "stop and go" intervals in clogged roads are chronically; an average poorly maintained Mexican car could run on an efficiency level of less than 15%!

Fig.4.6: Efficiency of the internal combustion engine (50kB)

Until the traditional combustion engine will be replaced by newer cleaner alternatives, like the Hydrogen Fuel Cell, the design of automobile engines is now being guided by requirements to reduce emissions of these pollutants.

5. Control Strategies

As in many other big cities of the world, Mexico City has made important efforts in order to reduce air pollution. Recognizing that transportation has proved to be a major pollution source within the Mexico City Metropolitan Area (ZMCM), any strategy that aims to reduce or control atmospheric pollution has to include a transportation improvement program. The main programs to combat air pollution in the ZMCM are:

- Reduce the use of private vehicles: To control the number of private cars in use at a given time, the government has implemented a one day stop program called "HOY NO CIRCULA" (today my car doesn't move).
- Stopping days are randomly distributed to encourage car owners to use public transport and/or adopt car-pooling.
- Control of vehicle conditions: As incomplete combustion in old or poorly maintained engines is a direct cause of carbon monoxide and unburned hydrocarbon emissions, the enforcement of engine maintenance standards has been another goal of ZMCM local government. The major compulsory program implemented in this direction is called the 'verification program'.
- Change of fuels: Many reformulated fuels have already been tested in the metropolitan area but only small changes in gasoline quality have been accepted so far. This is due mainly to the fact that current engine technology, combined with the meteorological and geographic characteristics of the Mexico City area are seen as the main reasons for high levels of ozone precursor emissions (and not fuel quality).
- Finally, some important successes already achieved in Mexico City have to be mentioned. Although these strategies alone will not bring air pollution under control, they are making an important contribution towards reducing it. The two major programs already working within the Mexico City Metropolitan Area are:
  - Reduction of lead and sulfur in fuels;
  - Compulsory implementation of catalytic converters.

5.a Urban Transportation System:

In order to reduce the fleet of fossil fuelled vehicles on the road, it is essential to pay special attention to the Urban Transportation System. It is thus not surprising that the collective transport subway net with its 11 lines, is one of the biggest transfer system in the world. The total length of Mexico City subway is currently 202km (that does not include a light rail line serving the southern part of the city with its 18 stations). All 11 lines are rubber tyred like some lines in Paris and the metros of Montréal and Santiago de Chile; except Line A which has standard steel track. It is one of the first systems that uses symbols and colors for identifying their metro stations and is by far the cheapest subway system in the world (1 ticket = US$0.15 as of July 1999).

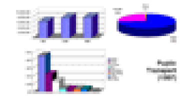

Fig.5.1: Public transportation (50kB)

Fig.5.2: D.F.'s Metro in operation (75kB)

Fig.5.3: D.F.'s Metro system (185kB)

Passengers: The number of passengers within the Metropolitan Area is continuously increasing, although the rate of increase is slowing (fig.5.1).
Reasons for using Public Transport: The main reason to travel is to move from home to work or school, and back again. Peak traffic occurs at 8:00, 14:00 and 18:00 hours on weekdays.
According to information provided by the city government, in 1997, most people travelled around Mexico City using public transportation (74%). It is important to note that private traffic is not only is about a quarter, but uses about ¾ of the total energy provided by PEMEX.
Although private cars are more common than any other type of vehicle on the roads (2,327,930), they are only used by a small portion of the total urban population. The most important transportation system for the majority of people within the ZMCM is the METRO (Metropolitan Transportation System) which carries more than 4 1/2 million passengers every day (fig.5.2.).
In addition to the **METRO** (fig.5.3), there are two other electric transportation systems:
i) a small tram network and the so-called **'light train'** which accounts for about 2% of journeys by the public.
i) there is also a **trunk system** transportation (mainly diesel engines) sponsored by the government of Mexico.

The objective of the Mexican government is to improve and regulate the suburban transport that circulates within the counties of the State of Mexico and in the Metropolitan Area. Furthermore, there are a considerable number of suburban buses powered by diesel engines. Many are in poor conditions, have old engines, and are poorly maintained. This is a general problem of most vehicles circulating on urban roads.

5.b IMECA

To provide information related to air quality conditions in the metropolitan area, the Mexican authorities have developed a pollution standard index called IMECA (from the Spanish 'Indice Metropolitano de la Calidad del Aire', fig.5.4). The index of the quality of the air, is defined as a representative although relative value of the levels of atmospheric contamination and its effects in the health within a certain region. Pollution levels exceeding 100 points on the IMECA scale are considered a threat to human health - see table.

Air Quality Summary for 1996: Some of the standards for air quality were exceeded in the ZMCM on 91% of days (333), including 71 days (19%) measured at more than 200 IMECA points and 5 days up to 250 points.
The **ozone** standard was exceeded on 89% of days (327) and for 20% of them the value of standard was doubled. Levels were exceeded on average on 75% of the days in each month. The $\mathbf{PM_{10}}$ standard was exceeded on 182 days (50%). **Nitrogen dioxide** went beyond the 100 IMECA point standard on 22% of days during the year. The highest value measured was approximately 160 IMECA points.
On eight days, **carbon monoxide** values went beyond the standard. The maximum value was almost 160 IMECA points. Due to an extraordinary situation caused by a natural gas shortage, fuel oil was burnt for two days in the ZMCM and concentrations above the standards set for sulfur dioxide were registered.
Levels of **lead** have been within air quality standards since 1995.
Carbon Monoxide (CO): Historical data for pollution at five specific parts of the city are available for ozone, carbon monoxide, sulphur dioxide, nitrogen dioxide and inhaled particles (PM10), pollution standard indexes (IMECA, Indice Metropolitano de Calidad del Aire), and lead concentration. 1996 data of polluted days above local standards.
Percentage of days greater or equal to 100 and 150 IMECA points are shown. Levels of 200 IMECA were reached on 5.2% of days for O_3 and none for PM10, CO, NO_2 and SO_2. This year the percentage of days greater or equal to 250 points was only reached for O_3 (0.3% days).

The graphic on the right shows the percentage of days for IMECA values above 100, 150 and 200. Values greater or equal to 250 IMECA during those years were observed mainly in 1991 (15) and 1992 (11). Values above 300 IMECA were observed in small percentages (1 or 3%) before 1994.

Particulate matter (PST, from the Spanish 'Particulas Suspendidas Totales') is manually monitored in the ZMCM. Its value frequently exceeds the accepted standards.

Concentrations of particulate matter smaller than ten microns (PM10) has been monitored since 1995. Standards were exceeded on 98 days during that year, and on 182 days during 1996.

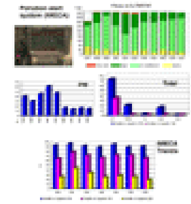

Fig.5.4: IMECA (140kB)

6. Conclusion

Prior to the 1940s, Mexico City was known for its clear air and spectacular views of snow-capped volcanoes. Today, the city's mountains are only rarely visible due to some of the worst air pollution in the World. Many factors have contributed to this situation national policies that have promoted industrial growth and a concentration of wealth and employment in Mexico's capital; a population boom from 3 million in 1950 to roughly 20 million today; and heavy reliance on motorized transportation. The city sits in a basin 2,240 meters above sea level, and is surrounded by mountains that rise one kilometer or more above the basin (a former lake bed). High elevation and intense sunlight are key factors in ozone formation. Air pollution is generally worse in the winter, when there is less rain and events of thermal inversion are more common.

Winds tend to blow across the city from the northeast, where a slight opening in the mountains allows moisture and winds from the Gulf of Mexico to enter the basin. These winds blow pollution from the region of heaviest industrial development towards downtown and the residential areas southwest of the city are pressed against the southern mountain chain.

Because of private interests, corruption, indulgence, ineptitude and decisions more political than scientific quick improvements have obstructed the fight against air pollution.

7. Literature

Atkins, P., Jones, L.; (1997); Chemistry; 3rd edition; W.H. Freeman & Co.; NY, USA
Brimblecombe P. (1986); Air composition and chemistry 2nd ed.; Cambridge Environmental Chemistry Series 6; Cambridge University Press, UK
Brown, L. T., LeMay, Jr. H. E.; (1977); Chemistry, the Central Science, Prentice Hall, Inc. Englewood Cliffs, New Jersey, USA.
Chang R. 1994; Chemistry 5th ed.; McGraw-Hill; New York, USA
Edgerton S.A, et al. (1997); Particulate Air Pollution in Mexico City; North American Research Strategy for Tropospheric Ozone; CDN, MEX, USA
Gloxhuber, C.; (1994); Toxicology; 5th ed.; Thieme Verlag; Stuttgart, FRG
Haider, M.; (1999); Lecture Script - Air analysis; Wacker Chemie; FRG
Hofmann, W.; (2001); Lecture Script - Aerosol Physics; University of Salzburg; AUT
Kisser, W.; (2000); Lecture Script - Toxicology; University of Salzburg; AUT
Lutgens, F., Tarbuck, E.; (1998); The Atmosphere; 7th Edition; Prentice Hall; NJ, USA
Mage D. et al. (1996) Urban Air Pollution in Megacities of the World; Atmospheric Environment Vol.30, No.5, pp681-686; Elsevier Science, UK
Meszaros E.; (1999); Fundamentals of Atmospheric Aerosol Chemistry; Akademiai Kiado, Budapest, HUN
Morawska, L.; (1999); Lecturing Script: Introduction of Aerosols; QUT, Brisbane, AUS
Reichl, F.; (1997); Taschenatlas der Toxikologie; Thieme Verlag; Stuttgart, FRG
Wilbraham, A. C., Staley, D. D., Matta, M. S.; (1998), Chemistry, Teacher's Edition, 4th edition, Addision-Wesley Publishing Company, New York, USA

BBC-World TV, Earth Report - City Smog (1999), UK - www.tve.org
National Geopgraphic, Mexico (1992), USA - NGTV

References on the WWW:

Urban Air Pollution in Mexico City
Mexico City lifts pollution alert
No relief for Mexico's air pollution crisis
Americas No let-up for Mexico City pollution
Americas Mexico City pollution emergency
San Antonio blames Bret, evacuees for air pollution
Sustainable Development Cases Studies
NAEC releases air pollution report
http://www.epa.gov/
INDOEX
http://www.epa.gov/oms/t2models.htm
http://www.epa.gov/epahome/faq.htm#jobs
Air Pollution Technology Fact Sheets
Information Center on Air Pollution
Air Pollution in Mexico City
Air Pollution & Lung Disease
Mexico City Fights Smog by Electrifying Air
PEMEX
Case Studies of Urban Air Pollution
life-threatening air pollution
The Great Smog Of 1952
Initiative for Sustainable Energy
Atmospheric Chemistry of Organic, Oxidants and Their Precursors