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Chemicals Aspects of Air Pollution

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INTRODUCTION

Pollution of the air may be regarded as the most critical for the simple reason it involves the air we breath in. Man can go without food or water for days and even weeks, but without air it becomes a matter of minutes. Over the years the general awareness on the importance of quality air has gained momentum and little wonder it has become a crusial issue in just about every country or areas accomposating sources of air pollution.

The history of air pollution probably dates back many thousand years, depending on how one may want to define it. However, history has recorded a royal proclamation from that of King Edward I of England (ca 1300), which goes:

"Be it known to all within the sound of my voice, whosoever shall be found quilty of burning coal shall suffer the loss of his head".

Queen Elizabeth I was reported to be annoyed by coal smoke and made complaints to the English Parliament in 1578. In 1875 the deaths of cattles in London was shown to be due to air pollution. But it was not until 80 years later in 1956 when the British Clean Air Act was passed. This was many years after the Meuse Valley disaster in Belgium (1930), the Donova disaster in Pennsylvania, USA (1948) and the London disaster in 1952. The USA Clean Air Act was

passed only in 1963. There had been various episodes of air pollution in recent history, the most important ones are shown in Table 1.

IMPORTANT TERMINOLOGIES

To fully understand air pollution, a few basic aspects of certain sciences are quite essential, notably chemistry, biology, geography and perhaps physics. However, the layman can be made to understand the essentials of air pollution with a little bit of self-education. As a branch of multi-disciplinary sciences, there are some important terms frequently used in discussions on air pollution, which are given in Table 2.

what constitute the air pollutants may exist in gaseous and particulate forms. The former include all obnoxious and toxic gases such as sulfur dioxide, oxides of nitrogen, and also ozone. Their concentrations are expressed in µg m⁻³ of air, i.e. based on the volume of air. Particulate air pollutants include all very fine particles found in the air, ranging in diameter from less than 0.01 µm to over 100 µm. The major ones, however range between 0.1 - 15 µm in diameter. Particulates in the air are frequently described in parts per million (ppm) or billion (ppb), i.e. based on a volume mixing ratio. Described on larger scales, there are also other expressions, such as tons per year.

What really constitute a "clean" as opposed to a "polluted" air is often subjective. Referring to some of the more important air pollutants, a ratio between clean and polluted air can be calculated,

Table 1: Important episods of air pollution

- 1. 1930 Presence of "smog" in the Meuse valley, Belgium, beginning 1st.
 December. The valley accommodates various types of industries,
 including steel, sulphuric acid, metals, glasses etc.
 Pollutants were trapped in the air due to temperature
 inversion.
 Casualties: 60 dead.
- Thick mist in the Donova urban area, Pennsylvania, USA, beginning on 26th. October, followed by temperature inversion. A heavily industrialised area. Casualties: 30 dead
- 3. 1950 "Smog" in Poza Rica, near Mexico City, Mexico. The city is located on a high altitude, with a narrower atmospheric level compared to the low lands.
 Casualties: unknown.
- 4.* 1950 Dusts pollution from grain mills cover the city of Minneapolis, Minnesota, USA.
 Casualties: unknown.
 - 5. 1952, Thick fog covering London between 5-9 December, 1952. Burning of coal added to the fine particulates and SO₂ in the air.

 Casualties: Additional 4000 death than normally expected. The phenomena occurred again in 1962 with lesser effects (due to Clean Air Act, 1956).
- 1953, Thick fog and temperature inversion in New York, in November 1962 (of 1953, 1962, 1966). Air was trapped together with air 1966. pollutants.
 Casualties: About 170 deaths.

- Dusts from the grain mills in New Orleans. Lousianna, USA, causing incidences of lung and respirator, diseases.
- 8. 1962 Photochemical smog in Los Angeles, California, USA. Thick smog receiving sun radiation resulted in photochemical processes in the air. Pollutants from automobiles and industries react under the influence of sun radiation.
- 9. 1970 Oxidation and accumulation of sulphate in the city of Tokyo, Japan.

- Table 2: Definition of some important terms, corresponding to those of the American Society for Testing and Materials in "Standards on Methods of Atmospheric Sampling and Analyses" (Quoted from Perkins, H.C. (1974) <u>Air Pollution</u>, McGraw-Hill Kogakusha Ltd., Tokyo).
- 1. <u>Particulate</u>: Particulate is a general term meaning "existing in the form of minute separate particles" (AP-49, 1969), either solid or liquid. Particulate is used interchangeably with aerosol.
- 2. <u>Aerosol</u>: A dispersion of solid or liquid particles of microscopic size in gaseous media, such as smoke, fog, or mist.
- 3. <u>Dust</u>: A term loosely applied to solid particles predominantly larger than colloidal, and capable of temporary suspension in air or other gases. Dusts do not tend to flocculate except under electrostatic forces; they do not diffuse, but settle under the influence of gravity. Derivation from larger masses through the application of physical force is usually implied.
- 4. <u>Droplet</u>: A small liquid particle of such size and density as to fall under still conditions, but which may remain suspended under turbulent conditions.
- 5. <u>Fly Ash</u>: The finely divided particles of ash entrained in flue gases arising from the combustion of fuel. The particles of ash may contain incompletely burned fuel. The term has been applied principally to the gas-borne ash from boilers with spreader stoker, underfeed stoker, and pulverized fuel (coal) firing.
- 6. <u>Fog</u>: A loose term applied to visible aerosols in which the dispersed phase is liquid. Formation by condensation is usually implied. In meteorology, a dispersion of water or ice.
- 7. <u>Fume</u>: Properly, the solid particles generated by condensation from the gaseous state, generally after volatilization from melted substances, and often accompanied by a chemical reaction such as oxidation. Fumes flocculate and sometimes coalesce. The term is popularly used in

reference to any or all types of contaminants, and in many laws or regulations, with the qualification that the contaminant have some unwanted action.

- Gas: One of the three states of aggregation of matter, having neither independent shape nor volume, and tending to expand indefinitely.
- 9. <u>Mist</u>: A term loosely applied to low-concentration dispersions of liquid particles of large size. In meteorology, a light dispersion of water droplets of sufficient size to be falling.
- 10. Particle: A small, discrete mass of solid or liquid matter.
- 11. <u>Smoke</u>: Finely divided aerosol particles resulting from incomplete combustion. Consists mainly of carbon and other combustible material.
- 12. <u>Soot</u>: Agglomerations of particles of carbon impregnated with "tar", formed in the incomplete combustion of carbonaceous material.
- 13. <u>Vapor</u>: The gaseous phase of matter which normally exists in a liquid or solid state.

as shown in Table 3. For instance, carbon monoxide (CO) and sulfur dioxide (SO₂) have very high ratios compared to carbon dioxide (C= $_2$), methane (CH₄) or ammonia (NH₃).

SOURCES OF AIR POLLUTION

The sources of air pollution are varied, with varying degree of importance depending on the target group. In urban or industrialised areas, the most common sources are transportation and the industries. Power stations, solid waste disposal and energy production are frequently important sources of air pollutant emissions. However, there are natural emissions of gases, eg. ${\rm CO_2}$ or ${\rm CH_4}$ from the earth. One such happening was the volcanic release of ${\rm CO_2}$ in Cameroon in 1986, which killed almost 1700 people. Here, ${\rm CO_2}$ can be classified as an air pollutant by virtue of its deadly effects on humans.

Table 4 gives some data on air pollution emission in USA, in 1974. It is obvious here that the most important source of oxides of sulfur is due to the stationary burning of fuels at power stations etc. This and transportation constitute the two most important sources of oxides of nitrogen. Transportation alone constitutes over 25% of carbon monoxide released into the air. Transportation also is the main contributor of hydrocarbons. Air particulates, however, are mainly emitted by industrial processes.

Table 3 : Comparisons of concentrations of gases in the air (ppm)

Gas	Clean Air*	Polluted Air**	Ratio
co ₂	320	400	1.3
СО	0.1	40 - 70	400-700
CH ₄	1.5	2.5	1.3
N ₂ 0	0.25	(?)	
03	0.02	0.5	25
so ₂	0.0002	0.2	1000
NH ₃	0.01	0.02	2

^{*}Source: Robinson, E., dan R.C. Robbins, 1972, In: Air Pollution Control, (Ed.) W. Strauss,

Part II, Wiley Interscience, N. York, pp. 1-93.

^{**}Source: Cadle, R.D. dan E.R. Allen, 1970, Science, vol. 167, pp. 243.

Table 4: Emission of air pollutants in U.S.A. (million tons per year, 1974)

Source	Oxides of sulfur	Oxides nitrogen	Hydro- carbon	Carbon Monoxide	Air particulates
Transportation	0.8	10.7	12.8 ,	73.5	1.3
Burning of fuel (stationary)	24.3	11.0	1.7	0.9	5.9
Industrial processes	6.2	0.6	3.1	12.7	11.0
Disposal of solids/wastes	0.0	0.1	0.6	2.4	0.5
Other sources		**	•		
(oil, gasoline production, etc.)	0.1	00.1	12.2	5.1	0.8
Total	31.4	22.5	30.4	94.6	19.5

Source: Environmental Protection Agency, in Council of Environmental Quality, Environmental Quality, 1975, p. 440).

IMPORTANT AIR POLLUTANTS

Sulfur dioxide

Coal-fired power stations constitue over 60% of the total SO₂ released in USA, based on a 1968 data (Perkins, 1974). Coal containing 2% sulfur can produce about 76 lb. of SO_2 per ton of coal burned. A modern coal-fired power plant on a 1000 megawatt rating can produce 76 x 10⁴ 1b of SO₂ per day. Thus, depending on the energy requirement of a state or area, an option for coal as opposed to other sources of energy resource due to economic reasons may guarantee the pollution of the surrounding air with SO2. Oil-fired power plants also generate SO2, depending on the sulfur content. The use of high rise chimneys result in the transportation of SO2, and other pollutants over large distances by the atmosphere. During this transport, oxidation processes i.e. oxidation of sulfur and nitrogen oxides to sulphuric and nitric acids, respectively, can happen resulting in the "acid rain" phenomena which may occur in another recipient country, as the European and American examples have shown. The acid rain in Scandinavian countries (Norway and Sweden) was found to be originated from continental Europe, and the acids released from north east USA migrated to deposit the problem in Canada: Sulfur is burnt along with the fossil fuel to generate the SO_2 and SO_3 (sulfur trioxide) formation. In the air SO_3 reacts with water vapour to form sulfuric acid, $\mathrm{H}_2\mathrm{SO}_4$. The rate of $\rm H_2SO_4$ and $\rm H_2SO_3$ (sulfurous acid) formation in the air increases if the air is also polluted with air particulates which provide the surface areas for chemical reactions.

The health and adverse effects of SO_2 are many. The most frequent report is the damage to human respiratory functions. Various studies, including the report from U.S. National Academy of Sciences (1974) relate SO_2 pollution with asthma, bronchitis and emphysema, and lung cancer. Additionally there are detrimental effects on plants, causing direct plant injuries, decreased photosynthesis process, stunting of growth etc. Fish kills have been reported in lakes affected with acid rain, and destabilization of fish species diversity in lakes. Structural effects have often been reported, the classic example being that of Taj Mahal, directly attributed to the obnoxious gases in the air. The US Environmental Protection Agency (EPA) Standards for SO_2 are $80~\mu g~m^{-3}$ on annual average basis, and $365~\mu g~m^{-3}$ on the 24 hour average basis. The Horld Health Organization (WHO) long term goal is $60~\mu g~m^{-3}$ on the annual mean basis, with 98% of measurements less than $200~\mu g~m^{-3}$.

Oxides of nitrogen

Nitrogen oxides are usually written as NO_{X} . The pollutant nitrogen oxides are nitric oxide, NO and nitrogen dioxide NO_{2} . However, the most abundant nitrogen oxide in the atmosphere is nitrous oxide, $\mathrm{N}_{2}\mathrm{O}$, which is chemically rather unreactive and not normally considered as a pollutant. Chemical conversions to NO occur in the air regardless the origin of the nitrogen oxide: burning of fuel or releases of nitrogen to the air from fertilizer, or even from the waste water or sewage treatment plants.

The US EPA ambient air quality standard for NO_2 is 100 μg m⁻³ based on annual average. The typical ambient air concentration of NO_X are normally within 10 - 200 μg m⁻³ in urban areas and <40 μg m⁻³ (Harrison, 1983).

The role of NO_{X} is important in smog formation and the photochemical smog reactions. It is also an important component of acid rain, via the oxidation of NO_{2} to nitric acid (HNO_{3}). Figure 1 illustrates the main features of the NO_{X} cycles. In the soil there are nitrogen transformations via processes known as nitrification, ammonification and denitrifications. Nitrogen gases N_{2} and N_{2} 0 can be released to the atmosphere from the soil, to undergo chemical processes which can generate NO and NO_{2} . The subsequent formation of nitric acid (HNO_{3}) can result in the acid rain, deposited to the ground, which again is subjected to the various nitrogen processes in the soil with the aid of bacteria.

The health effects of NO_{X} are on the respiration, damages to the bronchial tube and the lungs. NO_{2} can interfere with oxygen flow in the blood. The damages to plants, fish and buildings are commonly reported. Soils acidified due to the acid rain can cause a string of effects, from nutrient uptake, phosphate precipitation and hence its inavailability to plants, root damage and generally the loss of fertility affecting plant growth.

Carbon Monoxide (CO)

Urban CO levels are often higher than the rural areas, and

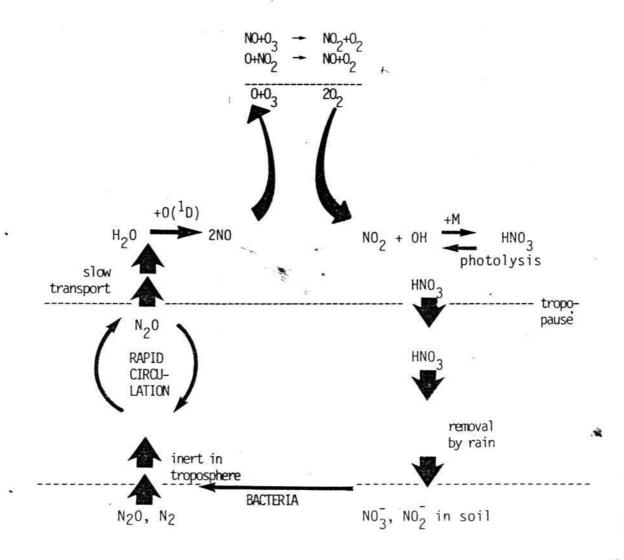


Fig. 1: Main features of the NO_X cycle with sources and sinks.

(Source: Donovan, R.J. (1983) Pollution pathways in the atmosphere, <u>In</u>: Harrison, R.M(Ed.) Pollution:

<u>Causes</u>, <u>Effects</u> and <u>Control</u>, Royal Society of <u>Chemistry</u>, U.K.P. 187.

remain an urban problem simply due to its main source, i.e. automobile emissions. In rural areas, the important sources of CO are agricultural burning, forest fires and perhaps solid wastes disposal. Car exhaust gases contain several percent CO under normal running conditions. When cold and chocked, the CO levels are much higher. The US EPA ambient air quality standard for CO is 10 ppm based on 8 hour average and 40 ppm based on 1 hour average. However, urban CO concentration may reach 50 ppm under heavy traffic with poor air circulation or ventilation (Harrison, 1983) or even 400 ppm under very heavy traffic (Ehrlich et al., 1981). Removal of CO from the air is somewhat a problem because the major sink of CO is the atmospheric oxidation to carbon dioxide (CO₂), which is a rather slow process

CO is often referred to as the "silent killer", due to its colourless, odourless and tasteless characteristics. This gas acts on the haemoglobin, the $\mathbf{0}_2$ carrier in the blood. CO has about 200 times the affinity of $\mathbf{0}_2$ for haemoglobin. This means that CO can displace $\mathbf{0}_2$ very readily from the haemoglobin molecule. Disruption in $\mathbf{0}_2$ supply to the various parts of the human body causes a variety of health effects, and even deaths in very high concentrations.

Hydrocarbons

The urban areas are again easily subjected to hydrocarbon pollution from the automobile emissions, industrial emissions and partial combustion of fuels.

There are actually over 200 hydrocarbon compounds found in

some polluted air. However, the important ones are those classified as "reactive" hydrocarbons, which take part in photochemical smog formation, and the carcinogenic hydrocarbons causing cancer in humans. Methane is the most abundant hydrocarbon in tha air. Lumped together hydrocarbons are considered important pollutants. In specific cases we find that benzene are highly toxic to humans, while ethane are damaging to growing plants. The important aspect of hydrocarbon is its role in photochemical smog reactions which generate a host of detrimental effects. Benzepyrine, for instance, has been related to lung cancer.

0zone

oxides of nitrogen and hydrocarbons, and hence is considered as a secondary polutant. Its concentration in photochemical smogs may exceed 400 ppb. The USA EPA ambient air quality standard for ozone is 120 ppb, not to be exceeded as an hourly average more than once per year. Adverse health effects on humans have been reported, as well as detrimental effects on plants and crops.

Air Particulates

Particles more than 10 micron in size fall to the ground, but those less than 10 micron remain suspended in the air, transported to other places. They may combine with rain water or mists and eventually fall to the ground. These air particulates may be water soluble or insoluble. What constitute these particulates are many

but mainly man-made materials. These include elemental and organic carbon, and iron oxides from corrosion processes and materials from surface erosion processes. In the urban areas, the main source of air particulates is the combustion of fossil fuels, the most important being coal.

The air particulates may easily effect the respiratory process, causing or enhancing respiratory diseases including lung cancer. Asbestos fibers had been long ago related to chronic lung diseases and lung cancer. Polynuclear aromatic hydrocarbon (PAH), an organic component of combustion-derived particulate is a known carcinogen.

The US EPA ambient air quality standard for total suspended particulates is 75 μg m⁻³ (annual geometric mean) and 260 μg m⁻³ (24 hour average), not to be exceeded more than once per year.

Lead (Pb)

Lead is a heavy metal which deserves merit to be discussed and studied on its own, due to its exceptional importance being a pollutant in the air, drinking water, fresh and processed foods, and even baby milk. Lead is a neuro-toxin, causing brain damage at high concentration, with a cumulative effect in the human body. It is a much feared heavy metal. It is also often classified as an occupational hazard. The U.K. Health and Safety Commission (1978) listed various types of work regarded as significant in terms of lead expossure in the UK, which is reproduced in Table 5.

Table 5: Work regarded as significant in terms of lead exposure in the UK

Types of lead work where there is liable to be significant exposure to lead (unless adequate controls are provided)

Examples of industries and processes where such work could be carried out

Lead dust and fumes

High temperature lead work (above 500°C)
 E.g. lead smelting, melting, refining, casting and recovery processes.

Lead burning, welding and cutting

- Work with lead compounds which gives rise to lead dust in air.
 E.g. any work activity involving a wide variety of lead compounds (other than low solubility lead compounds).
- Abrasion of lead giving rise to lead dust in air.
 E.g. dry discing, grinding, cutting by power tools.
- Spraying of lead paint and lead compounds Other than paint conforming to BS 4310/68 and low solubility lead compounds.
- Lead alkyls
 - Production of concentrated lead alkyls
 - 2. Blending of lead alkyls into gasolines
 - Entry into fixed or mobile plant and vessels, e.g. road tankers, rail tankers or sea tankers carrying leaded gasoline, e.g. for inspection, cleaning and maintenance purposes.

- lead smelting and refining; non-ferrous metals, e.g. gun metal, leaded steels manufacture; scrap metal and wirepatenting processes.
- of lead coated and painted plant and surfaces in demolition work; shipbuilding, breaking and repairing; chemical industry; miscellaneous industries.
- manufacture of lead batteries, paints and colours, lead compounds, rubber products, glass, pottery, manufacture and use of lead arsenate as pesticide (agriculture and allied work).
- manufacture of detonators (explosives industry).
- miscellaneous industries e.g. motor vehicle body manufacture and repair of leaded car bodies, firing of small fire arms.
- painting of bridges, buildings etc. with lead paint.
- lead alkyl manufacture.
- blending processes at oil refineries.
- plant and vessel entry at oil refineries, at transport terminals and any place where such work is carried out.

(Source: Health and Safety Commission (1978). Control of lead at work, Draft Regulations and Draft Approval Code of Practice, Hm So, London).

Lead is added as an additiive to petrol as an anti-knock agent to optimise octane ratings in motor-engines. It is released from the exhaust in organic forms to remain as a particulate, deposited on surfaces of leaves or vegetables grown near roadsides or in the urban areas. Lead can also be deposited to the soils and taken up by plants via root uptake. Lead from the air can be deposited into the aquatic environment near urban areas, to be taken up by the aquatic lives, including fish.

LOCAL SITUATION

Studies on air pollution in Malaysia has largely been confined to the Kuala Lumpur area. Studies on CO by the Department of Environment (DOE) in 1981 showed that from sampling stations at eleven different roads in Kuala Lumpur gave maximum values of 50 ppm and minumum of 0.1 ppm. The average values range between 4.6 - 18.8 ppm. Studies by Inouye (1987) on several air pollutants in Kuala Lumpur show interesting results. Figure 2 shows the diurnal variations in NO, NO₂ and O₃ between the months of April - May 1985. The NO concentration reaches its peak in the morning between 7.00 - 9.00 am, coinciding with the morning rush hour, and again at 20.00 hours, i.e. accumulation from the late afternoon rush hour. The build up of NO₂ takes up after 10.00 am and remains somewhat constant at about 20 ppm until 22.00 hours. However, ozone levels peak in the afternoon between 12.00 to 16.00 hours, at other times staying at lower concentration.

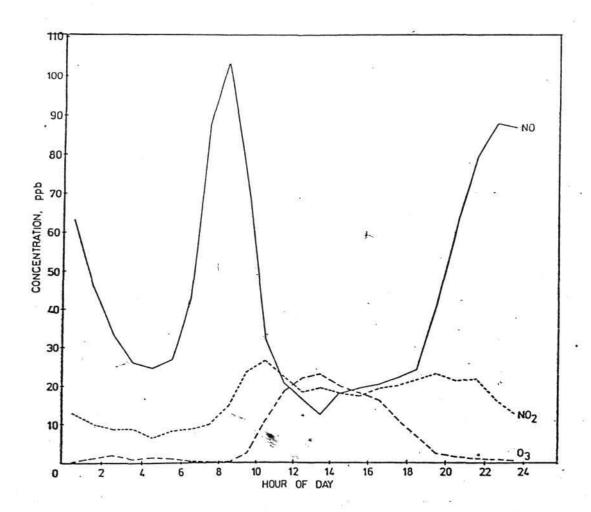


Fig 2: Diurnal variations in nitric oxide, nitrogen dioxide and ozone, Kuala Lumpur (April-May, (1985).

(Source: Inouye, 1986).

Inouye's observation is quite similar to that of Leighton (1961) for the Los Angeles basin during the photochemical smog (Fig.3). In this case, the NO_2 levels build up after the NO_2 start to decrease early in the morning, while ozone takes up after noon. The hydrocarbon levels are highest in the morning, decreasing with the rest of the day.

Inouye (1987) also compared the NO_X levels with SO_2 , CO and suspended particulate matter (SPM), as shown in Fig. 4. The NO_X , SPM and CO fluctuations are quite similar, in giving the highest peak in the morning (7.00 - 9.00 hours) and evening (20.00 - 24.00 hours). The evening peaks are due to the accumulation from the morning emission and additional injection from the evening rush hour. SO_2 , however, is highest in the morning (about 9 ppm) going down to about 2 ppm in the afternoon and rising slightly to about 4 ppm in the late afternoon.

Several studies have been done on Pb and other heavy metals in the Kuala Lumpur environment (such as Badri, 1984a, b, c; 1986a, b; Badri and Sham, 1986, 1987). Part of the results of these studies is shown in Table 6 for Pb and other metals found in several media or sinks in and around the Kuala Lumpur city area. The results indicate a serious problem with Pb in the city environment, which is attributed primarily to the automobile emission. Pb in petrol in Malaysia is quite high at 0.84 ppm. A legislation has been passed to reduce the lead level to 0.4 ppm by January 1st., 1986.

The high accumulation of Pb and other pollutants in the Kuala Lumpur city is also influenced by the restrictions on air flow in the Klang Valley. This is illustrated in Fig. 5, which shows that

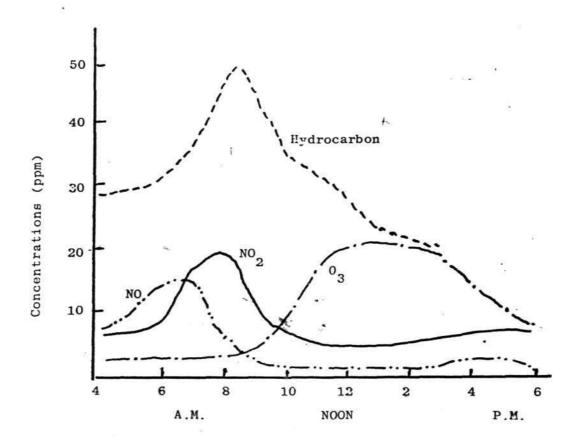


Fig. 3 Variations of the components of photochemical smog in the Los Angeles basin.

(modified from Leighton, 1961).

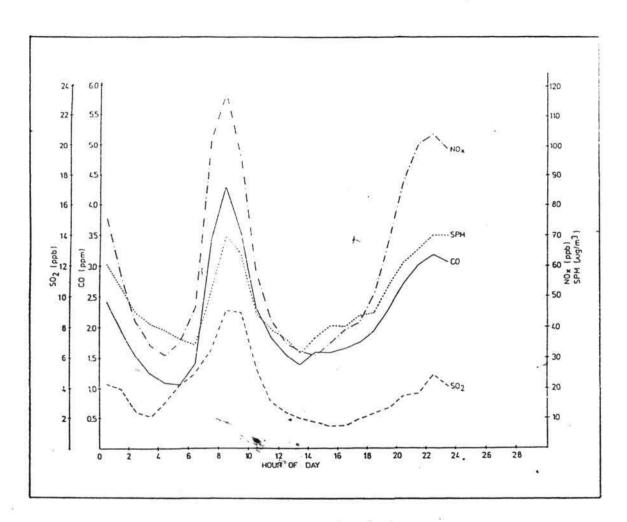
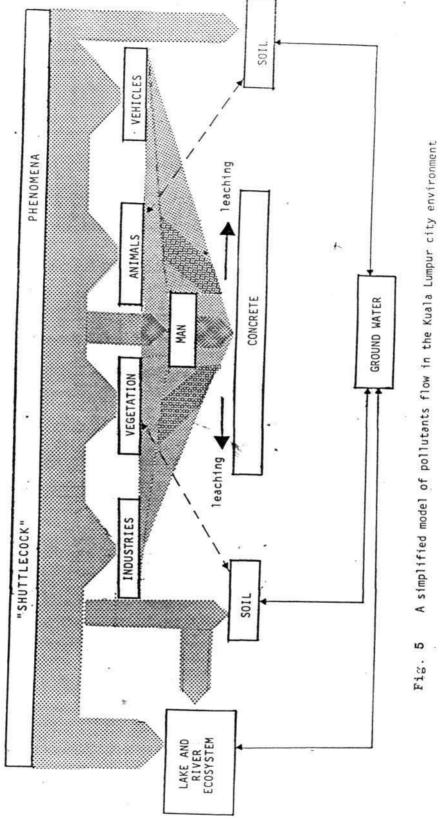


Fig. 4: Diurnal variations in oxides of nitrogen, SPM, carbon monoxide and sulphur dioxide concentrations in Kuala Lumpur (April 10 - May 5, 1985).

(Source: Inouye, 1987).



Range of total metal concentrations in roadside soils and dusts within the Kuala Lumpur city area, and rural Malaysian soils (in µg g⁻¹). Table 6:

			Soils	Soils	Average	O cano
a A	Koadside soils, innercity	Dusts, innercity	City Highway	KL-Seremban Highway	M'sian Soils	Shale *
P	500-2,500	. 550-7,200	200-4,000	40-	12	. 50
Zn	350-2,000	210-1,020	40-1,000	10-1,200	20	92
3	3-60	15-120	,05-9	7-100	2.0	45
PS	0.5-12	3-5	1-1	2-8	0.2	0.3
As	8-34	ţ	•		1.2	ī
. Hg	0.3-15	,	•	1	0.3	0.2
Fe .	8,000-35,000	500-4,000	2,500-30,000 2,000-80,000	,000,08-000	•	(4.72%)
Ř	200- 3,000	100- 300	500- 2,000	20- 2,500		009

* Turekian and Wedepohl (1961)

Source: Badri and Sham (1987).

man is the final recepient of pollutants emitted by the automobiles, industries etc. enhanced by the "shuttle cock phenomena". This is referred to the restricted wind flow pattern in the Klang Valley, resulting in the transport of air back and forth from Kelang to the city area depending on the land/sea temperature differences. The city also suffers from frequent temperature inversion, and the heat island phenomena. This aspect has been described in more detail by Sham (1979, 1987).

CONCLUSION

Air pollution is certainly an important aspect of environmental degradation which deserve proper attention on the part of the city planners, local government and the government, generally. It affects human lives and other resources. Tragic episodes of air pollution have happened affecting human health and lives, and measures should be taken to avoid such thing from occurring in Malaysia. It is important for the general public to be educated on the principles involved in the chemistry and physics of air pollution. The awareness on air quality is essential because air is something shared by everyone.

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