1 THE PROBLEM - AIR POLLUTION

1.1 HISTORICAL REMARKS

Ambient air composition over the earth has undergone several changes throughout history. In particular, there is evidence (Chambers, from Stern, 1976) that "the primeval gaseous environment probably contained almost no free oxygen" and that "oxygen in more recent years has accumulated as a result of photosynthetic processes utilized by early nonoxygen-dependent species." Those early living species have either disappeared, as a consequence of these changes, or adapted.

Anthropogenic activities, especially since the 14th century, when coal began to replace wood as the prime source of energy, have provided a clear "perturbation" of the earth's environmental balance. In the atmosphere, these anthropogenic pollutants have often generated locally unhealthful air quality and, sometimes, lethal air pollution concentrations, as during the well-known London episode of December 1952. In addition to short-term episodic effects, atmospheric pollutants are known to generate long-term adverse effects, which are, however, difficult to forecast.

The emergence of petroleum products in this century has characterized a new industrial revolution. In 1945, it was recognized that petroleum products are responsible for a new type of "smog," a photochemical summertime smog, first discovered in the Los Angeles area. Photochemical smog is quite different from the traditional wintertime sulfur smog (the "London" smog) typically generated by the combustion of sulfur-containing fuels, such as coal.

The last decade has been characterized by a growing interest in long-range air pollution transport phenomena and global effects. First in northern Europe and then in eastern North America, it has been shown that large emissions of "primary" pollutants, such as sulfur dioxide (SO_2), undergo chemical transformations in the atmosphere. These transformations generate, hundreds or thousands of kilometers downwind, new chemical species known as "secondary" pollutants, such as the sulfates (SO_4^{2-}). These secondary species are responsible for new adverse affects, such as acidic deposition (or, as commonly and improperly called in the media, acid rain).

Two "global" issues have recently become a major concern: 1) the "greenhouse" effect, which could cause an increase of the earth's average temperature as a consequence of increasing concentrations of carbon dioxide (CO_2), a species that has never been considered a "pollutant" and whose huge emissions have never been controlled; and 2) the possible depletion of the stratospheric ozone layer, a natural protective "blanket" from harmful solar radiation, by certain species emitted by anthropogenic activities. On the subject of global issues, the "nuclear winter" hypothesis should also be mentioned, i.e., the possibility that large fires, following a nuclear war, may inject large amounts of particles into the atmosphere, generating a substantial and prolonged decrease of earth's temperatures.

Other air pollution problems that have recently emerged are (Urone, from Stern, 1986): indoor air pollution, in particular, asbestos; nuclear accidents, especially after the Chernobyl disaster; nonionizing radiation, which seems to cause physiological disfunctions; risk assessment, especially for the characterization and prevention of accidental releases of toxic pollutants (e.g., in the form of heavy gases that have unique dispersion characteristics); and atmospheric visibility and its impairment by air pollutants.

It has often been pointed out that government pollution control action has seldom (or perhaps never) anticipated adverse effects and that only large-scale disasters or environmental deterioration have provided stimuli for effective action and preventive measures. Recent years, however, seem to be characterized by increasing public concern, at least in the western societies, about environmental issues and by the pressure of public opinion on government and industry for major preventive control actions and for the implementation of emergency/accident contingency plans.

1.2 WHAT IS AN AIR POLLUTANT?

Which substances must be considered air pollutants? Or, better, which substances, emitted into the atmosphere, can be considered safe, nonpolluting compounds? The question is certainly not an easy one, since the term "air pollution" can have many definitions.

Williamson (1973) gave a satisfactory clarification of this problem, by elaborating the difference between a "pollutant" and a "contaminant." A contaminant was defined as "anything added to the environment that causes a deviation from the geochemical mean composition." On the other hand, a pollutant, to be considered such, must be a contaminant responsible for causing some adverse effect on the environment.

Clearly, the distinction between pollutants and contaminants is based on our limited understanding of short-term and long-term adverse effects of each chemical compound. Moreover, this evaluation is complicated by chemical reactions that can transform a contaminant into a pollutant. We can, therefore, say that any contaminant is a potential pollutant and that, in many cases, the two words are synonymous.

An example of the above difference is given by the CO_2 gas that is abundantly emitted into the atmosphere from anthropogenic combustion processes. CO_2 does not present adverse effects to living organisms and was, therefore, considered only a contaminant. Measurements have shown, however, that ambient CO_2 concentrations throughout the world are constantly increasing, which reveals an accumulation in the atmosphere of a considerable fraction of the CO_2 emitted by anthropogenic activities. Since further CO_2 concentration increases are expected to induce an increase in the average temperature of the earth, CO_2 should be considered, in this respect, a pollutant. (See Chapter 13 for further discussion on the CO_2 problem.)

Air pollutants are found in the form of

- gases, e.g., sulfur dioxide (SO_2)
- particulate matter, e.g., fine dust

and are injected into the atmosphere from

- natural sources, e.g., volcanoes, ocean spray, pollen
- anthropogenic sources, e.g., industrial, commercial, agricultural, transportation activities

These "primary" pollutants (i.e., those directly emitted from sources) undergo chemical reactions that result in the subsequent formation of other species, i.e., "secondary" pollutants, in the form of

- gases, e.g., ozone (O_3)
- particulate matter, e.g., sulfates (SO_4^{2-})

One of the most important factors characterizing the atmospheric particulate matter is the size (e.g., the diameter) of the particles. Particles are called

- coarse particles, when their diameter is larger than 2.5 μm

- fine particles (or respirable particulate matter, RPM), when their diameter is less than 2.5 μm; fine particles can also be divided into two modes: the nuclei mode, with diameter below 0.1 μm, and the accumulation mode, with diameter greater than 0.1 μm
- inhalable particles (or inhalable particulate matter, IPM), when their diameter is less than 10 μm

Coarse particles are generally less important, since their large mass causes fast gravitational removal from the ambient air, and are less harmful to the human species, because they are easily removed by the upper respiratory system. Fine particles are more important because of their adverse effects on human health and visibility.

Particles in the atmosphere can also be classified, independently from their size, as

- viable particles (such as pollen, fungi, bacteria, etc.)
- nonviable particles

1.3 POLLUTANT EMISSIONS

1.3.1 Primary Gaseous Pollutants

The primary gaseous emissions of air pollutants are the following (Urone, from Stern, 1976 and 1986)

- sulfur compounds (e.g., SO_2, H_2S)
- nitrogen compounds (e.g., NO, NH_3)
- carbon compounds (e.g., hydrocarbons HC, CO)
- halogen compounds (e.g, fluorides, chlorides, bromides)

1.3.2 Primary Particulate Matter

The primary particles in the atmosphere are

- air ions, with diameters much smaller than 0.1 μm, formed, for example, from solar and cosmic radiation, radioactive material and combustion processes
- Aitken nuclei (i.e., particles smaller than 0.1 μm in diameter) and fine particles between 0.1 and 2.5 μm, formed by natural processes, such as sea spray and forest fires, and by industrial combustion processes

- carbonaceous materials, made up of soot, including elemental carbon and organics
- particles from automotive emissions, mostly lead in the form of oxide, sulfate or bromochloride
- particles containing light metals, such as sodium, magnesium, aluminum, silicon, potassium and calcium
- particles containing heavy metals, such as titanium, vanadium, chromium, manganese, iron, nickel, copper, zinc, arsenic and selenium
- large particles, such as dust and sand transported by wind, particulate matter from industrial activities, or rising dust from off–road transportation
- viable particles, such as pollen, micro–organisms, and insects

Also, since atmospheric particles are hygroscopic in nature, they acquire water to equilibrate to a given humidity.

The sources of particulate matter (Hidy, 1984) are:

- extraterrestrial sources, which only slightly affect concentrations in the planetary boundary layer, but contribute largely to the concentrations of extraterrestrial dust found above 30–40 km height.
- sea salt emissions, generated by the oceans from breaking waves, wind action on the wave crests, or bubbles of foam breaking on the water surface
- suspension of soil dust, from the action of wind or vehicles on loose soil areas
- volcanic eruptions
- forest and brush fires
- anthropogenic emissions, from combustion of fuel and waste, and industrial activities

1.3.3 Radioactive Pollutants

Radioactivity is a primary air pollutant (Eisenbud, from Stern, 1976) from both natural and anthropogenic sources. Natural radioactivity results from the presence of radionuclides, which originate either from radioactive minerals in the earth's crust or from interaction of cosmic radiation with atmospheric gases. Anthropogenic radioactive emissions originate from

- nuclear reactors

- the atomic energy industry (mining, milling, and reactor fuel fabrication)
- nuclear or thermonuclear bomb explosions
- plants reprocessing spent reactor fuel

1.3.4 Secondary Gas Pollutants

Atmospheric chemical reactions (especially the photochemical ones) are responsible for the transformation of primary pollutants into intermediate reaction products (e.g., free radicals) and, finally, into stable end products, the secondary pollutants. The major gaseous secondary pollutants are

- NO_2, formed from primary NO
- O_3, formed via photochemical reactions

A more complete discussion on this subject is presented in Chapter 9.

1.3.5 Secondary Particulate Matter

Atmospheric chemical reactions (especially the photochemical ones) are responsible for the transformation of primary and secondary gaseous pollutants into secondary particles. The main known processes are

- the transformation of SO_2 into sulfates, SO_4^{2-}
- the transformation of NO_2 into nitrates, NO_3^-
- the transformation of organic compounds into organic particles

Secondary particulate matter consists mainly of fine particles (smaller than 2.5 μm), which are in the respirable range and have the potential to adversely affect human health and visibility.

1.3.6 Global SO_x and NO_x Emissions

Sulfur emissions, mainly SO_2, have represented, and still represent, the major and most common air pollution problem throughout the world. SO_2 emissions are responsible for (1) the "London" winter–type smog, (2) several lethal air pollution episodes, and (3) acidic deposition effects associated with sulfate transport and deposition.

The worldwide use of coal and oil as combustion fuels, especially for electric power production, is the major anthropogenic source of SO_2. An initial estimate of worldwide SO_2 emission was given by Robinson (from Strauss, 1972) as about 133 Tg a^{-1}(*). Cullis and Hirschler (1980) gave a more complete evaluation of the atmospheric sulfur emission budget and cycle. Their results are presented below.

The global atmospheric sulfur cycle is qualitatively described in Figure 1-1. Cullis and Hirschler (1980) provided detailed estimates of the various components of the cycle, as shown in Table 1-1, which gives the total annual natural emissions of atmospheric sulfur (in Tg S a^{-1}) and Table 1-2, which presents the anthropogenic emissions of SO_2 from 1965 to 1976 (in Tg SO_2 a^{-1}).

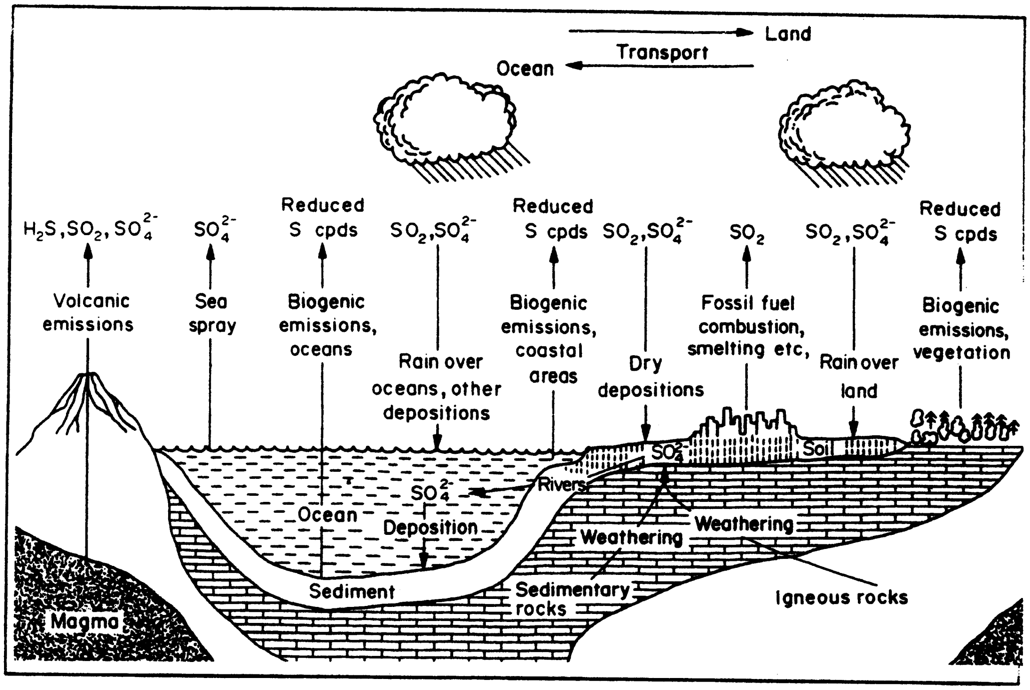

Figure 1-1. The atmospheric sulfur cycle (from Cullis and Hirschler, 1980). [Reprinted with permission from Pergamon Press.]

(*)Tg a^{-1} means 10^{12} grams per year.

Table 1–1. *Estimates of natural emissions of atmospheric sulfur (in Tg S a^{-1} = 10^{12} grams per year) (from Cullis and Hirschler, 1980; see this paper for the references mentioned in this table). [Reprinted with permission from Pergamon Press.]*

		Removal processes ($Tg\,a^{-1}$)		Emission processes ($Tg\,a^{-1}$)						
							Biogenic emissions			
Authors	Total	Precipitation	Dry deposition*	Volcanoes	Sea-spray	Man-made	Sub-total	From sea	From land	Net transfer from land to sea ($Tg\,a^{-1}$)†
Junge (1963a)	315	140	175		45	40	230	160	70	− 95
Eriksson (1963)	365	200	165		45	40	280	170	110	− 65
Robinson and Robbins (1972)	212	129	83		44	70	98	30	68	+ 64
Kellogg *et al.* (1972)	184	159	25	1	44	50	89	18	71	+ 60
Friend (1973)	217	143	74	2	44	65	106	48	58	+ 33
Bolin and Charlson (1976)	143			3	44	65	31	28	3	− 1
Hallberg (1976)	149			3	44	65	37	34	3	− 7
Granat (1976)	144	106	38	3	44	65	32	27	5	+ 2
Garland (1977)‡	266	112	154		44	70	152	46	106	+ 84
Davey (1978)§	200	123	77	10	44	60	86	26	60	+ 60

*Where subtotals are given only for the combined effects of precipitation and dry deposition, 20% of the sulphur is assumed to be removed by dry deposition, by analogy with nuclear fall-out (Junge, 1963b; Friend, 1973).

†The values are calculated by adding biogenic emissions from land areas to those from volcanoes and due to man and subtracting biogenic emissions from sea and those due to sea-spray.

‡The distribution between land and sea has been calculated on the basis of the percentages used by Robinson and Robbins (1972) in their estimates, from which the data of Garland (1977) originate.

§Somewhat similar estimates are given in an earlier paper by Davey (1973).

Table 1-2. *Anthropogenic sulfur emissions (Tg SO_2 a^{-1})* (from Cullis and Hirschler, 1980; see this paper for the references mentioned in this table). [Reprinted with permission from Pergamon Press.]*

	1965	1970	1974	1975	1976
Coal					
Hard coal	71.4 (47.9)	77.5 (45.0)	81.1 (43.3)	85.5 (45.4)	88.1 (42.5)
Lignite	28.1 (18.9)	30.5 (17.7)	31.6 (16.9)	32.8 (17.4)	33.1 (16.0)
Coal coke	2.4 (1.6)	2.5 (1.5)	2.5 (1.3)	2.5 (1.3)	2.6 (1.2)
Subtotal	102.0 (68.5)	110.4 (64.1)	115.2 (61.5)	120.8 (64.2)	123.8 (59.7)
Petroleum					
Refining	5.7 (3.8)	6.8 (4.0)	5.8 (3.1)	5.5 (2.9)	7.3 (3.5)
Motor spirit	0.3 (0.2)	0.4 (0.2)	0.5 (0.3)	0.5 (0.3)	0.6 (0.3)
Kerosene	0.2 (0.13)	0.1 (0.05)	0.1 (0.04)	0.1 (0.04)	0.1 (0.04)
Jet fuel		0.05 (0.03)	0.1 (0.06)	0.1 (0.06)	0.1 (0.06)
Distillate fuel oil	2.0 (1.3)	2.2 (1.3)	3.0 (1.6)	2.8 (1.5)	3.8 (1.8)
Residual fuel oil	20.3 (13.6)	29.8 (17.3)	37.4 (20.0)	34.3 (18.2)	45.8 (22.1)
Petroleum coke		0.4 (0.2)	0.4 (0.2)	0.5 (0.3)	0.6 (0.3)
Subtotal	28.5 (19.1)	39.6 (23.0)	47.2 (25.2)	43.8 (23.3)	58.3 (28.1)
Non-ferrous ores					
Copper	12.9 (8.7)	15.8 (9.2)	18.4 (9.8)	17.5 (9.3)	18.8 (9.1)
Lead	1.5 (1.0)	1.7 (1.0)	1.6 (0.9)	1.5 (0.8)	1.6 (0.7)
Zinc	1.3 (0.9)	1.2 (0.7)	1.1 (0.6)	1.0 (0.5)	1.0 (0.5)
Subtotal	15.7 (10.5)	18.8 (10.9)	21.1 (11.3)	20.0 (10.6)	21.4 (10.3)
Others					
H_2SO_4	1.6 (1.1)	2.1 (1.2)	2.5 (1.3)	2.4 (1.3)	2.5 (1.2)
Pulp/paper	0.4 (0.2)	0.5 (0.3)	0.5 (0.3)	0.5 (0.3)	0.5 (0.2)
Refuse	0.65 (0.4)	0.65 (0.4)	0.65 (0.3)	0.65 (0.3)	0.65 (0.3)
Sulphur	0.05 (0.04)	0.03 (0.02)	0.05 (0.03)	0.05 (0.03)	0.05 (0.02)
Subtotal	2.7 (1.8)	3.2 (1.9)	3.7 (2.0)	3.6 (1.9)	3.7 (1.8)
Total	148.9†	172.2‡	187.3	188.2	207.2

*The figures in brackets represent percentages of the total.

†This is a previous value for coal, petroleum and non-ferrous ores (Robinson and Robbins, 1972), to which emissions from other sources have been added.

‡This may be compared with the value of 166 Tg SO_2 predicted for 1970 (Peterson and Junge, 1971).

The main conclusion is that, according to the 1976 estimates, the anthropogenic emissions of sulfur are 104 Tg *S* a^{-1}, over 40 percent of all atmospheric sulfur emissions, and are expected to exceed the natural emissions before the end of the present century.

A recent reevaluation of SO_x and NO_x emissions (actually, only those from fossil-fuel combustion) is provided by Hameed and Dignon, 1988), who also reveal interesting trends in the geographical variations of these emissions from 1966 to 1980. Through the calculations of two regression models, they provide the annual global emissions of SO_x (in Tg *S* a^{-1}) that are shown in Figure 1-2. These emissions, however, are approximately half of those estimated

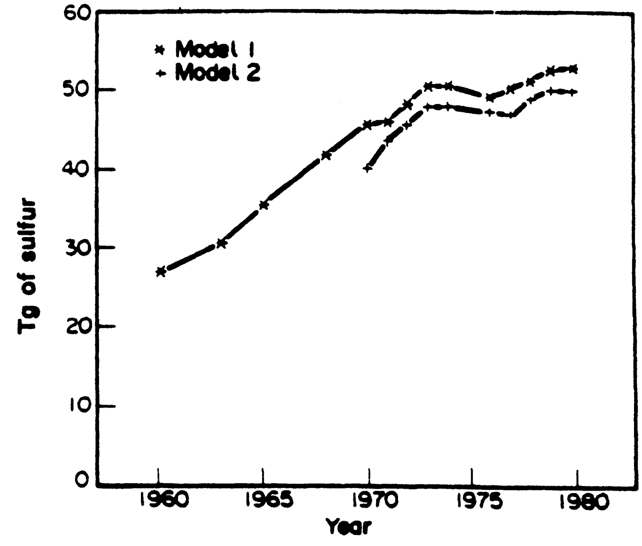

Figure 1-2. Annual global emissions of SO_x from fossil-fuel combustion in Tg of S estimated by Model 1 (upper curve) and Model 2 (lower curve) (from Hameed and Dignon, 1988). [Reprinted with permission from Pergamon Press.]

by Cullis and Hirschler (1980), a fact which evidences the uncertainties in these difficult evaluations.

Hameed and Dignon (1988) also provide trends of NO_x emissions from fossil fuel combustion, which are summarized in Figure 1-3. Their regional analysis also shows that, although the greatest rates of SO_x and NO_x emissions occur in the northern midlatitudes, the greatest increases from 1966 to 1980 have taken place in the tropics, a fact that is having dramatic consequences in the deterioration of urban air quality in third world cities around the world.

1.3.7 Air Pollution Emissions and Air Quality Trends in the United States

Recent studies (e.g., U.S. EPA, 1980, 1985, and 1988) have provided detailed information on air pollution emissions in the United States, which is generally not available for other countries. We summarize here some of the important anthropogenic emission data and trends in the United States (from U.S. EPA, 1988).

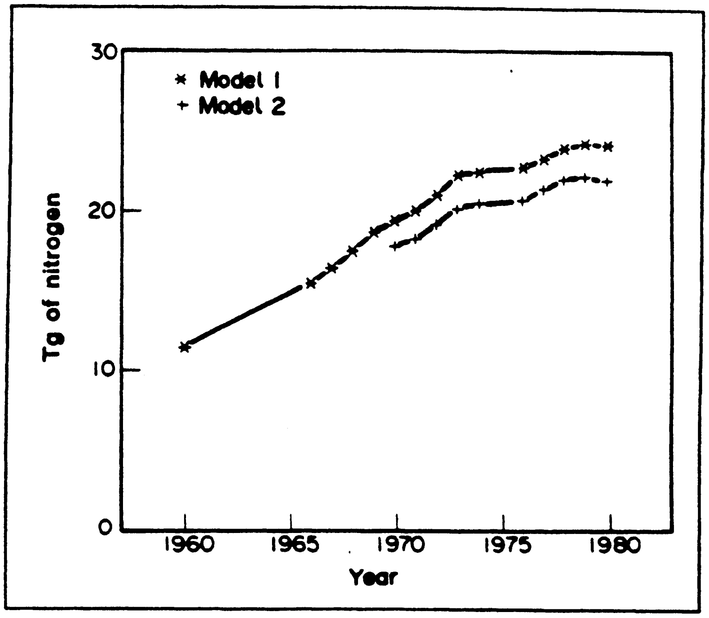

Figure 1-3. Annual global emissions of NO_x from fossil-fuel combustion in Tg of N estimated by Model 1 (upper curve) and Model 2 (lower curve) (from Hameed and Dignon, 1988). [Reprinted with permission from Pergamon Press.]

- **Particulate Matter**

Annual average total suspended particulate (TSP) levels, which have been measured at 1,435 locations, decreased 23 percent between 1977 and 1986, while TSP emissions varied from 9 Tg a^{-1} to 7 Tg a^{-1}. In 1987, the U.S. EPA promulgated new standards for particulate matter using a new indicator, PM_{10} (i.e., inhalable particles with aerodynamic diameters smaller than 10 μm), instead of TSP. This new standard focuses on particles responsible for adverse health effects and, therefore, future U.S. EPA trends will be based on PM_{10} data, collected by PM_{10} monitoring networks being deployed nationally.

- **Sulfur Dioxide, SO_2**

Annual average SO_2 levels measured by 302 continuous monitors decreased 37 percent from 1977 to 1986. Emissions of SO_2 decreased from 27 Tg a^{-1} in 1977 to 21 Tg a^{-1} in 1986. Historic SO_x emission data from 1900 to 1980 can be found in Gschwandtner et al. (1986) and trend analyses of monthly SO_2 emissions are given by Lins (1987).

- **Carbon Monoxide, CO**

The second highest non-overlapping 8-hour average CO concentrations measured at 182 sites have shown a decrease of 32 percent between 1977 and 1986. This decrease is due to the implementation of pollution controls for mobile sources. Emissions of CO varied from 82 Tg a^{-1} in 1977 to 62 Tg a^{-1} in 1986.

- **Nitrogen Dioxide, NO_2**

Annual average NO_2 concentrations, measured at 111 sites, increased from 1977 to 1979 and then generally decreased through 1986. Measurements in 1986 were 14 percent lower than the 1977 levels. The NO_x emissions have shown a similar trend, remaining in the range of 19–21 Tg a^{-1}. Los Angeles, California, is now the only area in the United States that exceeds the annual air quality standard (53 ppb). Historic NO_x emission data from 1900 to 1980 can be found in Gschwandtner et al. (1986).

- **Ozone, O_3**

The composite average of the second highest daily maximum 1-hour ozone values, recorded at 242 sites, decreased 21 percent from 1977 to 1986, probably due to the combined decrease of NO_x emissions and of volatile organic compound (VOC) emissions, which declined from 24 Tg a^{-1} in 1977 to 19 Tg a^{-1} in 1986.

- **Lead, Pb**

The composite maximum quarterly average of ambient lead concentrations, recorded at 82 urban sites, decreased 87 percent between 1977 and 1986, while lead emissions decreased 94 percent (from $140 \cdot 10^3$ metric tons a^{-1} to $8 \cdot 10^3$ metric tons a^{-1}). This large decrease is mostly due to the reduction of the lead content of leaded gasoline.

1.4 ADVERSE EFFECTS

A vast literature describes the adverse effects of atmospheric pollutants on the environment and on ecology; e.g., Williamson (1973, Chapter 2), Stern (1977a), National Research Council (1983, Chapter 1; for acidic deposition effects), and, especially, Stern (1986). The October 1988 issue of *Atmospheric Environment* was dedicated to human exposure to air pollutants. Adverse effects include the following.

- **Odor**

Ambient atmospheric pollutants can cause disturbing odors, characterized by their quality and intensity. In particular, human beings have a low threshold for sulfur-bearing compounds and these are, therefore, easily detected.

- **Human Health Effects**

Several adverse effects on human health have been identified, especially respiratory effects (bronchitis, pulmonary emphysema and lung cancer). Some pollutants (such as ozone) have possible mutagenic effects, while others have shown carcinogenic effects (see Table 1-3). Pollutants also have synergistic effects, in which, for example, SO_2 damage to the human respiratory system can be greatly enhanced by the presence of fine particles.

- **Materials Damage**

Pollutants damage materials and structures by abrasion, deposition/removal, direct/indirect chemical attack and electrochemical corrosion (Tombach, 1982). Especially in the European countries, air pollution damage to artistic buildings and materials (e.g., marble and statues) is significant. Table 1-4 gives a summary of these effects.

- **Ecological Damage**

Vegetation shows clear damage due to ozone, sulfur dioxide, nitrogen dioxide, fluoride, peroxyacetic nitrate (PAN) and ethylene. Domestic and dairy animals have suffered deleterious effects during several pollution episodes. Livestock damage has been occasioned by fluoride (from heavy chemical industry emissions) and arsenic (e.g., from copper smelters).

- **Meteorological Changes**

On a larger scale, pollutants affect meteorological parameters, as illustrated in Table 1-5. Visibility is impaired by attenuation of solar radiation (urban turbidity), NO_2 absorption of light and particle light scattering. For the latter, small particles, with a size comparable to the wavelength of light (0.40 to 0.70 μm), are the most effective.

- **Effects of Acidic Deposition**

Acidic deposition is a phenomenon in which acidic substances like H_2SO_4, HNO_3, and HCl are brought to earth by dry and wet deposition. This deposition

Table 1-3. Unit risk factors for analysis of inhalation exposure (adapted from the SCAQMD, 1988). These unit risk factors are those developed by the California Department of Health Services for those substances identified as toxic air contaminants by the California Air Resources Board. The unit risk factor is the probability that an individual will contract cancer when exposed, through inhalation, to one $\mu g/m^3$ *of a substance over a lifetime (70 years). The weight of evidence classifications are: A, human carcinogen; B, probable human carcinogen (B1, limited human evidence; B2, sufficient animal evidence, but inadequate or no human evidence).*

Substance	CAS Number	Unit Risk Factor $(\mu g/m^3)^{-1}$ and Weight of Evidence
Acrylonitrile	107–13–1	6.8×10^{-5} [B1]
Allyl Chloride	107–05–1	5.9×10^{-6} [B2]
Arsenic	7440–38–2	4.3×10^{-3} [A]
Asbestos	1332–21–4	190×10^{-6} per 0.0001 fibers/cm^3 [A]
Benzene	71–43–2	5.3×10^{-5} [A]
Benzidene	92–87–5	6.7×10^{-2} [A]
Benzo(a)Pyrene	50–32–8	1.7×10^{-3} [B2]
Beryllium	7440–41–7	2.4×10^{-3} [B2]
Bis(2–chloroethyl)ether	111–44–4	3.3×10^{-4} [B2]
Bis(chloromethyl)ether	542–88–1	2.7 [A]
1,3–Butadiene	106–99–0	6.7×10^{-5} [B2]
Cadmium	7440–43–9	1.2×10^{-2} [B1]
Carbon tetrachloride	56–23–5	4.2×10^{-5} [B2]
Chlorinated dioxins and dibenzofurans (TCDD equivalent)		38 [B2]
Chlorinated ethanes: 1,2–Dichloroethane (Ethylene dichloride)	107–06–2	2.2×10^{-5} [B2]
Chloroform	67–66–3	2.3×10^{-5} [B2]
Chromium, hexavalent	7440–47–3	1.5×10^{-1} [A]

Table 1–3 (continued)

Substance	CAS Number	Unit Risk Factor $(\mu g/m^3)^{-1}$ and Weight of Evidence
Dichlorobenzidene	91–94–1	4.8×10^{-4} [B2]
2,4–Dinitrotoluene	121–14–2	1.9×10^{-4} [B2]
Diphenylhydrazine	122–66–7	2.2×10^{-4} [B2]
Ethylene dibromide	106–93–4	7.2×10^{-5} [B2]
Ethylene dichloride	107–06–2	2.2×10^{-5} [B2]
Epichlorohydrin	106–89–8	1.2×10^{-6} [B2]
Ethylene oxide	75–21–8	1.0×10^{-4} [B1]
Formaldehyde	50–00–0	1.3×10^{-5} [B1]
Hexachlorobenzene	118–74–1	4.9×10^{-4} [B2]
Hexachlorocyclohexane:		
technical grade	---	5.7×10^{-4} [B2]
alpha isomer	319–84–6	7.6×10^{-4} [B2]
Methylene chloride	75–09–2	4.1×10^{-6} [B2]
Nickel:		
refinery dust	---	2.4×10^{-4} [A]
subsulfide	0120–35–722	4.8×10^{-4} [A]
Nitrosamines:		
Dimethylnitrosamine	62–75–9	1.4×10^{-2} [B2]
Diethylnitrosamine	55–18–5	4.3×10^{-2} [B2]
Dibutylnitrosamine	924–16–3	1.6×10^{-3} [B2]
Phenols:		
2,4,6–Trichlorophenol	88–06–2	5.7×10^{-6} [B2]
Polychlorinated biphenyls	1336–36–3	1.2×10^{-3} [B2]
Trichloroethylene	79–01–6	1.3×10^{-6} [B2]
Vinyl chloride	75–01–4	2.7×10^{-6} [A]

Table 1–4. Air pollution damage to various materials (from Yocum et al. in Stern, 1986). [Reprinted with permission from Academic Press.]

Materials	*Types of damage*	*Principal damaging pollutants*	*Other environmental factors*	*Methods of measurement*	*Mitigation measures*
Metals	Corrosion, tarnishing	Sulfur oxides and other acid gases	Moisture, air, salt, particulate matter	Weight loss after removal of corrosion products, reduced physical strength, change in surface characteristics	Surface plating or coating, replacement with corrosion-resistant material, removal to controlled environment
Building stone	Surface erosion, soiling, black crust formation	Sulfur oxides and other acid gases	Mechanical erosion, particulate matter, moisture, temperature fluctuations, salt, vibration, CO_2, microorganisms	Weight loss of sample, surface reflectivity, measurement of dimensional changes, chemical analysis	Cleaning, impregnation with resins, removal to controlled environment
Ceramics and glass	Surface erosion, surface crust formation	Acid gases, especially fluoride-containing	Moisture	Loss in surface reflectivity and light transmission, change in thickness, chemical analysis	Protective coatings, replacement with more resistant material, removal to controlled environment
Paints and organic coatings	Surface erosion, discoloration, soiling	Sulfur oxides, hydrogen sulfide	Moisture, sunlight, ozone, particulate matter, mechanical erosion, microorganisms	Weight loss of exposed painted panels, surface reflectivity, thickness loss	Repainting, replacement with a more resistant material
Magnetic storage media	Loss of signal, tape failure	Particles	Moisture, abrasion, wear	Signal quality, physical and chemical analysis	Removal to controlled environment, periodic cleaning and recopying

Table 1–4 (continued)

Paper	*Embrittlement discoloration*	*Sulfur oxides*	Moisture, physical wear, acidic materials introduced in manufacture, microoganisms	Decreased folding endurance, pH change, molecular weight measurement, tensile strength	Synthetic coatings, storing in a controlled atmosphere, deacidification, encapsulation, impregnation with organic polymers
Photographic materials	Microblemishes	Sulfur oxides	Particulate matter, moisture	Visual and microscopic examination.	Removal to controlled environment
Textiles	Reduced tensile strength, soiling	Sulfur and nitrogen oxides	Particulate matter, moisture, light, physical wear, washing	Reduced tensile strength, chemical analysis (e.g., molecular weight), surface reflectivity	Replacement, use of substitute materials, impregnation with polymers
Textile dyes	Fading, color change	Nitrogen oxides, ozone	Light, temperature	Reflectance and color value measurements	Replacements, use of substitute materials, removal to controlled environment
Leather	Weakening, powdery surface	Sulfur oxides	Physical wear, residual acids introduced in manufacture	Loss in tensile strength; chemical analysis	Removal to a controlled environment, consolidation with polymers, replacement
Rubber	Cracking	Ozone	Sunlight, physical wear	Loss in elasticity and strength, measurement of crack frequency and depth	Addition of antioxidants to formulation, replacement with more resistant materials

Table 1-5. Approximate minimum concentration thresholds of atmospheric effects due to minor constituents (from Hobbs et al., 1974 as reported by Robinson in Stern, 1977a). [Reprinted with permission from Academic Press.]

		Threshold	
Species	*Effect*	*Volume per unit volume of air*	*kg/km³ of air*
Ice nuclei	Cloud structure and precipitation	10^{-18}	10^{-6}
CCN	Cloud structure and precipitation	10^{-15}	10^{-3}
Aerosols	Visibility and heating rates	10^{-12}	10^{0}
HCl, H_2SO_4	pH of rain	10^{-11}	10^{-2}
Aerosols	pH of rain	10^{-10}	10^{2}
NH_3	pH of rain	10^{-10}	10^{-1}
SO_2	pH of rain	10^{-8}	10^{1}
NO_2	Visibility and heating rates	10^{-7}	10^{2}
O_3	Heating rates	10^{-6}	10^{3}

affects primary receptors (e.g., the surface of soil with no vegetation), secondary receptors (e.g., soil underneath vegetation), and tertiary receptors (e.g., lakes receiving water from runoff from the watershed). Lakes located in both North America and Northern Europe are very sensitive to acid deposition because of their limited buffering capacity. These lakes, when exposed to acid precipitation pass through three stages (Havan, in Stern, 1986), as illustrated in Figure 1-4. The first stage (bicarbonate lakes) is characterized by a steady decrease in the acid-neutralizing (i.e., buffering) capacity. The second stage (transition lakes) begins when the acid-neutralizing capacity is exausted and concentrations of sulfate and metals begin to increase. During the third and final stage (acid lakes), the pH begins to stabilize. By this stage, however, acid-sensitive species have been eliminated. Acidified lakes remain ideal for many recreational activities except fishing.

• Effects of Carbon Dioxide, CO_2

On a global scale, there is widespread concern that the increasing anthropogenic CO_2 emissions from combustion processes, and the consequent global increase of CO_2 concentrations, may increase the average temperature of the earth, as illustrated in Table 1-6. Preindustrial (i.e., 1860) CO_2 levels are commonly thought to have been between 270 ppm and 290 ppm. The present levels are about 330 to 340 ppm, with recent growth rates of more than 1 ppm per year.

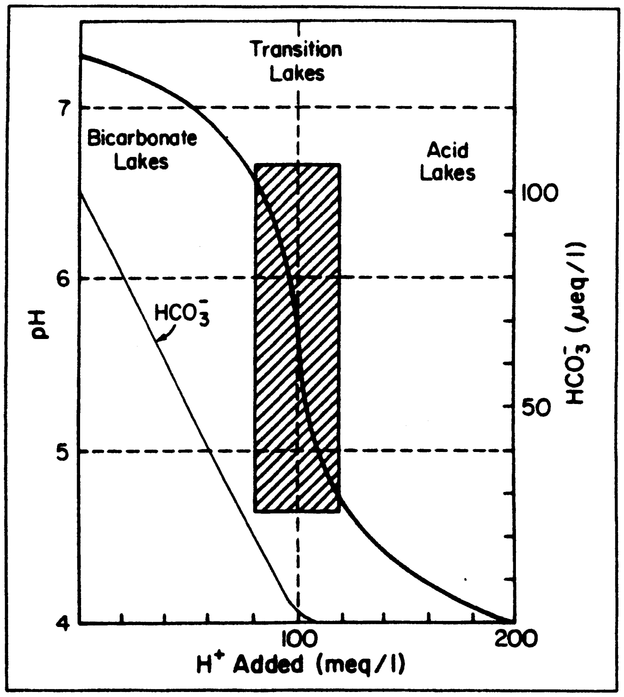

Figure 1-4. *Titration curve for a bicarbonate solution with an initial concentration of 100 μEq/liter (from Henriksen, 1980). [Reprinted with permission from Pergamon Press.]*

A range analysis for possible future growth of CO_2 ambient concentration is presented in Figure 1-5. (See further discussion on the CO_2 problem in Chapter 13).

- **Effects on Stratospheric Ozone**

Another possibly adverse effect on a global scale is the reduction of stratospheric ozone caused by chlorofluorocarbons, which are stable in the troposphere but are photodissociated in the stratosphere. A reduction of stratospheric ozone would decrease the efficiency of the present protective "blanket" that limits the amount of ultraviolet solar radiation that reaches the earth's surface. (See further discussion on stratospheric ozone in Chapter 13).

1.5 AIR QUALITY LEGISLATION

Several countries in the world have established air pollution laws and regulations and have implemented air quality and/or emission standards. The

Table 1-6. Estimated range of CO_2-induced temperature rise (in °C) (from U.S. EPA, 1980).

	Low Latitude (0°-5°)		Average		High Latitude (80°-90°)	
Atmospheric CO_2 compared to preindustrial levels	O	P	O	P	O	P
2x	0.8	2.4	1.5	2.9	3.6	11
4x	1.9	4.8	2.9	5.8	7.5	18
6x	2.8	6.0	4.1	7.5	9.0	20

O = optimistic; P = pessimistic.

Source: Adapted from Markley, O.W., et al., Socio-political Impacts of Carbon Dioxide Buildup in the Atmosphere Due to Fossil Fuel Combustion, prepared for the U.S. Energy Research and Development Administration, 1977, p. 35.

United States, in particular, has developed a large and complex body of air quality laws directed toward the goals of progressive air quality improvement in those regions characterized by unhealthy concentration levels and environmental preservation in regions with clean air (especially the national parks in the West). Moreover, the U.S. regulations have incorporated the use of several air quality diffusion models as official regulatory tools (e.g., to be used for the authorization of new emissions of air pollutants).

Air quality legislation (or lack of it) has affected the development of air pollution modeling techniques in different countries. In the United States, the air quality regulations, together with the existence of a free market typically oriented toward consulting business activities, have created the proper conditions for the development of "practical" techniques, sometimes very sophisticated ones, but still based on methods that rely upon available data and limited computational resources. In general, U.S. studies have benefited from public and private funding sources and have focused on specific problems with a clear goal-oriented inclination.

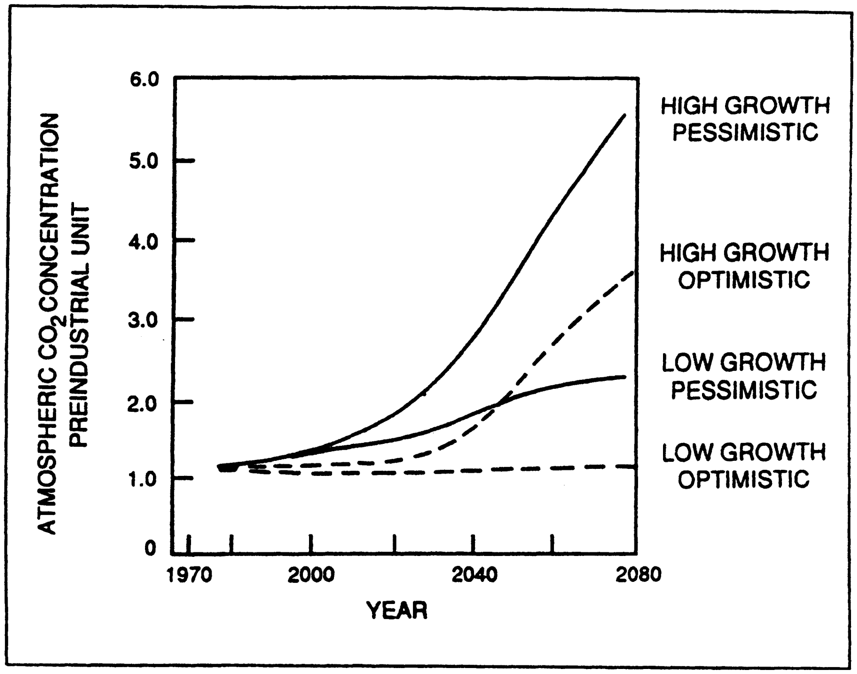

Figure 1-5. Atmospheric carbon dioxide concentrations — range analysis (from U.S. EPA, 1980).

European studies and research activities in this field have been carried out mainly by public organizations, i.e., universities and research centers. However, research centers of private industries have also provided valuable contributions. European research, performed without the pressure of specific legislative goal-oriented objectives, has covered with success interesting and advanced topics. These activities, however, have not yet finalized a set of transferable computer packages like those in the United States.

In long-range transport problems, national legislation is not sufficient and international rules and agreements need to be found. This seems to be a sensitive issue in northeastern North America, where Canada is blaming the United States for a large fraction of their acidic deposition, and in Europe, where many countries are blaming each other for the same issue. The Chernobyl accident has shown everyone that air pollution, unlike people, can freely emigrate from one country to another, and affect even countries like Italy, which many meteorologists believed well-protected by the Alpine mountain chain.

In spite of progress in the last two decades toward economical and political unity in Europe, common environmental legislation is still lacking. The recent common trend of increasing the average height of industrial emissions (especially in power plants) is certainly improving the near-field air quality, but is expanding the effects of long-range transport and acidic deposition all over Europe. As an example of this trend, Figure 1-6 shows that the strong reduction of low- and medium-level SO_2 emissions in the United Kingdom has been associated with almost a doubling of high-level SO_2 emissions during the same period, 1960 to 1980. In the absence of unified legislation, most countries may be tempted in the

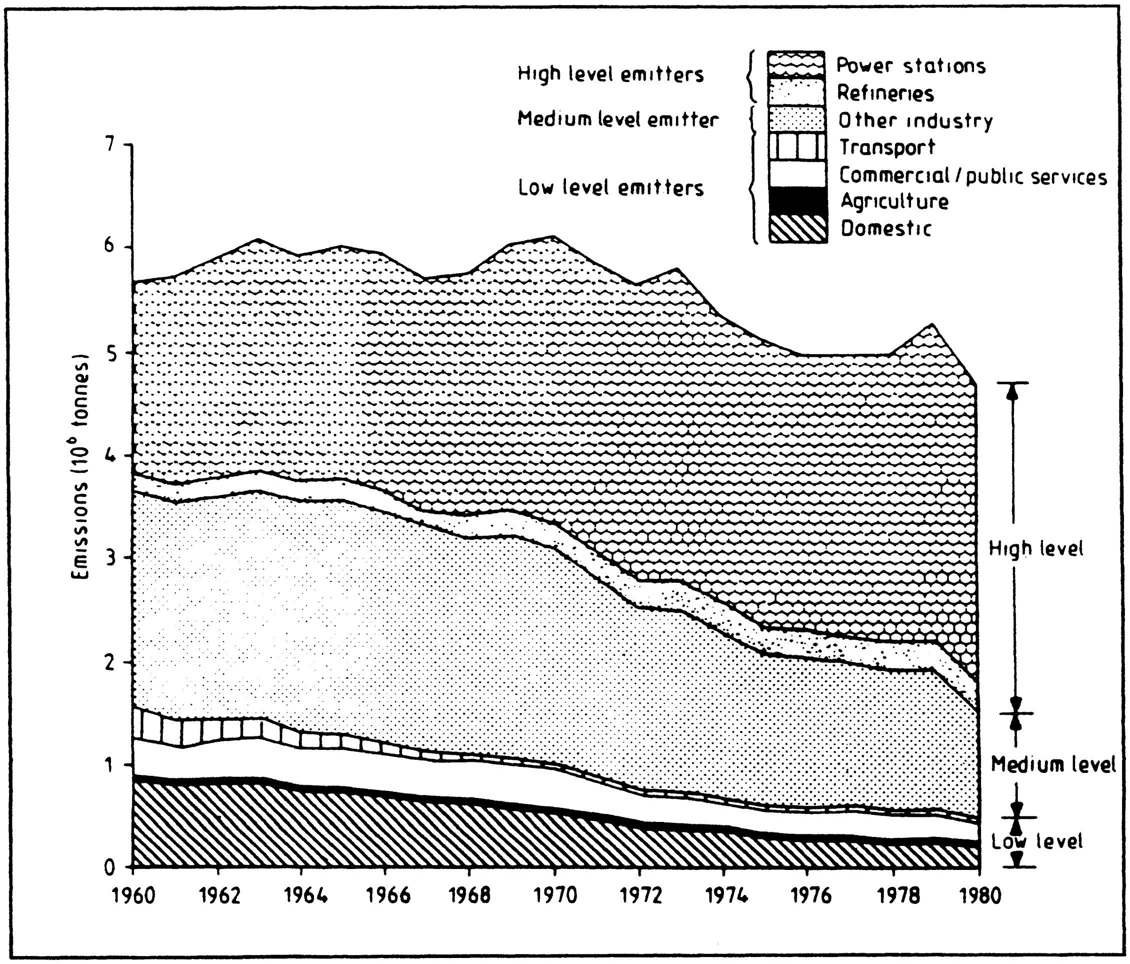

Figure 1-6. Trends in UK sulphur dioxide emissions as a function of height of emission. Data from Warren Spring Laboratory Reports, *as presented by Henderson-Sellers (1984). [Reprinted with permission from IOP Publishing, Ltd.]*

near future to continue increasing emission rates and release heights, thus further increasing their pollution of neighboring nations. Joint European R&D modeling efforts are expected, in the next few years, to provide legislators with suggestions and recommendations for a unified set of European environmental regulations.

Several articles and books have reviewed air quality legislation, especially in the United States. Stern (1977b) presents the national and worldwide air quality management problems and air pollution standards (see, in particular, Heath and Campbell in Stern, 1977b, for air pollution legislation and regulation). Historical review of U.S. air quality laws can be found in Stern (1977c; 1982). Controlled trading, which represents the most recent and, probably, innovative development toward a "free market" approach for air pollution control, is also discussed in U.S. EPA (1981)(*) and Ryan (1981). A review of air pollution legislation and regulation in the European community is provided by O'Riordan (1989).

(*) More information on recent EPA regulations can be obtained from Regulatory Reform Staff, U.S. Environmental Protection Agency PM-223, Washington, D.C. 10460, U.S.A.; telephone (202) 287-0750.

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