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by

T. Cvitas, H. Gusten

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CHEMISTRY OF ATMOSPHERIC POLLUTION

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STRUCTURE OF THE ATMOSPHERE

The atmosphere of the earth consists of a mixture of gases which completely envelop our planet and follow its rotation. The air is connected to the earth mainly by gravitational forces and only in higher layers, i.e. above 1000 km. the electromagnetic interactions become dominant. The total mass of the atmosphere is approximately 5×10^{18} kg. and represents only one millionth part of the mass of our planet. However, the atmosphere is very important for development of the earth and particularly for development and existence of life. The atmosphere protects the earth surface from high energy radiation from the universe, either by reflexion or by absorption in higher layers.

Radiation from the sun corresponds quite closely to radiation of a black body. Maximum energy is radiated in the visible band which correspond to a temperature of 5700°K at the sun's surface. Most of that radiation passes through the atmosphere and is absorbed on the surface of the earth. The earth, however, being a significantly cooler body, emits mostly in the infrared radiation band where many atmospheric components, such as H₂O and CO₂, absorb very strongly. Thus by absorbing infrared radiation, the atmosphere prevents cooling of the planet, which is most significant at night. This phenomenon is known in literature as the "greenhouse effect", though in greenhouses there is another dominant mechanism i.e. prevention of convection (1).

According to literature the atmosphere can be divided into a few layers (fig. 1). Next to the earth's surface, up to the

altitude of about 10 kilometers there is a layer referred to as the troposphere. Here, the air gets warmed by absorption of infrared radiation, by direct contact with the warmer surface of the earth and by friction due to flow of air currents. The temperature falls with altitude from about 20°C on the surface to about -50°C at the upper limit of the troposphere i.e. in the tropopause. The layer above the tropopause i.e. at the altitudes of about 10 to 50 km. is referred to as the stratosphere. In lower stratosphere the temperature is approximately constant at about -50°C . At altitudes beyond 30 km. the temperature starts rising and reaches about 0°C at the upper limit of the stratosphere - in the stratopause. This rise in temperature is caused by ozone, which almost completely absorbs sun radiation in the wavelength range from 210 to 310 nm. Above the stratopause, and up to the altitude of 80 km. is the mesosphere. Here, there is again a negative temperature gradient and the temperature in the mesopause drops to -80°C . Above the mesopause, in the so called thermosphere the temperature suddenly rises, though because of the degree of rarefication the concepts of the kinetic theory of gases may no longer apply. While below the mesopause, the changes in the pressure, temperature and density (at about 80 km.) depend mainly upon meteorologic conditions, at higher altitudes, the dominant factors are solar activities.

According to its composition, the atmosphere may be divided into the homosphere, up to the altitude of 100 km., which has an approximately constant composition of air, and the heterosphere, above 100 km., where separation of gases occurs due to gravitation. In the thermosphere there is a larger proportion of ionized

particles which are formed due to intensive shortwave radiation. Consequently, because of its composition this layer is also referred to as the ionosphere.

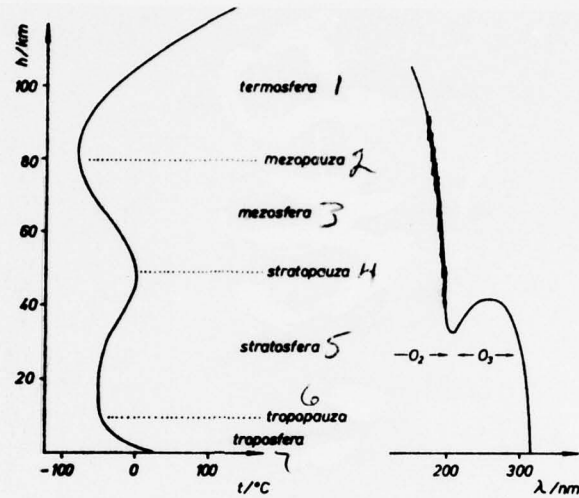


Fig. 1 - /1/ thermosphere; /2/ ^Smezopause; /3/ ^Smezosphere; /4/ ^{STRA TOPAUZE;}stratopause; /5/ stratosphere; /6/ tropopause; /7/ troposphere

- Temperature (t) and ultraviolet radiation in the earth's atmosphere as a function of altitude (h).

The curve on the right illustrates altitudes that can be penetrated by radiation of intensity I_0/e . I_0 is the intensity of the sun's radiation outside of the atmosphere and is dependent upon its wavelength (λ)

In higher layers the interactions with radiation are rather complex. Consequently, we will discuss in the following text only the lower atmosphere i.e. the troposphere and the stratosphere.

Weather changes take place primarily in the troposphere.

A vertical exchange of air masses takes place due to hydrostatically unstable conditions due to elevated temperatures, and horizontal exchanges of air masses occur due to winds. Sometimes, such exchanges cause formation of temperature inversions

where the **warmest** layers of air are found at altitudes between 200 and 2000 m. (fig. 2). In such cases the air above the surface of the earth forms a hydrostatically stable system within which vertical exchange is drastically reduced. This favours accumulation of various pollutants in the atmosphere. In Zagreb, appearance of inversions is relatively frequent (3) in any season. It is thus not surprising that periods² of intensively polluted air are frequently observed.

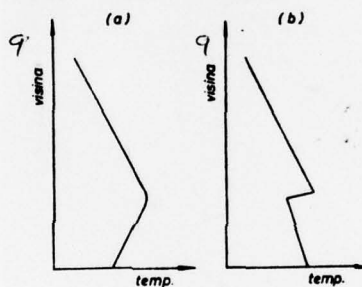


Fig. 2. - /9/ altitude

- Temperature inversion: (a) low level and (b) high altitude.

Two interesting problems of the atmosphere have been given little attention by scientists: 1. its origin and development and 2. its composition. Consequently, very little is today known about these problems. While major components of the atmosphere are in most cases listed in order of their concentrations, a closer analysis reveals that with exception of the noble gases, all atmospheric gases participate in complicated cycles (4).

Such cycles include a large number of various physical, chemical and biological processes. The sources could be volcanic or similar geological activities, biological and chemical processes in the atmosphere and industrial and other human activities. On the other side, gases also disappear from the atmosphere due to various processes such as precipitation in the hydro- or lithosphere, chemical and biological processes in the atmosphere or on the surface of the earth or by diffusion into the upper layers to the point of escaping into interplanetary space.

The residence time of various gases in the troposphere varies considerably. Some are accumulated during ecological time (Ar, Ne, Kr, Xe, N₂) while concentration of others remained approximately constant. They could be regarded as being in a pseudo-stationary state. Gases with volume (or molar) proportions* exceeding 10⁻⁸ are listed in Table 1 and are grouped according to their cycles (4).

*The volume proportion ϕ of a gas (i) in the air is equal to the ratio of the volume of that gas (V_i) and the total volume of all components of the air $\phi_i = v_i / \sum_j V_j$ at equal temperature and pressure. For an ideal gas the volume proportion is equal to the partial (molar) amount ($x_i = n_i / \sum_j n_j$, represents the amount of the j-th component. Volume proportion of a pollutant is usually of the order of magnitude of 10⁻⁶ or less. Thus it is often expressed in parts per million (ppm) or parts per billion (ppb). More rarely it is given as pphm (parts per hundred million) for 10⁻⁸ and ppt (parts per trillion) for 10⁻¹². To avoid confusion it is important to note the English and European continental system of numbers differ. While we use million, billion and trillion for 10⁶, 10⁹ and 10¹² and 10¹⁸ they represent 10⁶, 10⁹ and 10¹² in the English system, respectively.

Table 1. Cycles of more important atmospheric gases /page 247

/1/ Gas; /2/ Volume proportion $\times 10^6$; /3/ Residence time in the troposphere; /4/ Cycle; /5/ do not participate in cycles; /6/ biological cycle prevalent; /7/ variable ; /8/ days to weeks; /9/ inflow prevalently biological, outflow prevalently physico-chemical; /10/ physico-chemical cycle prevalent.

Plin 1	Volumni udjel 10^6 2	Vrijeme zadržavanja u troposferi 3	Ciklus 4
Ar	8300		ne sudjeluju u ciklusima 5
Ne	18		
Kr	1,1		
Xe	0,09		
N ₂	78×10^6	10 ⁶ a	pretežno biološki ciklus 6
O ₂	21×10^6	10 ⁶ a	
CO ₂	315	15 a	
CH ₄	1,1	5 a	
H ₂	0,4	5 a (?)	
N ₂ O	0,25	10 a	
CO	0,1	0,2 a	
H ₂ S/SO ₂	var. ?	dani do tjedni 8	izvori pretežno biološki, odvodi pretežno fizičko-kemijski 9
NH ₃	var. ?		
NO/NO ₂	var. ?		
CH ₃	var. ?		
H ₂ O	var. ?	10 d	pretežno fizičko-kemijski ciklus 10
O ₃	var. ?	0,3 a	
He	5,2	10 ⁷ a	
Rn	var. ?	3 d	

The troposphere thus represents an enormous container within which a series of complex processes are taking place. Under the influence of radiation many pollutants decompose into very reactive radicals which react farther with other ingredients in the air. Aerosols are formed, which often act as catalysts for new chemical reactions. Particulates and soluble gases are washed out of the atmosphere by precipitation and thus it is exactly because of the great activity of the troposphere that its composition has not been historically significantly changed even in the presence of various sources of strange gases. Only in recent times

have human activities become so large that they started to effect the composition of the atmosphere. This is particularly noticeable in regions of dense habitation and large concentration of industry.

TROPOSPHERIC POLLUTANTS

Increase in ^{the} concentration (participation) of certain matters or particulates in the atmosphere can have detrimental effects on human health, on animal and plant world and on many technological materials. Such gases or particulates are referred to as pollutants and are classified as primary and secondary, depending upon the manner in which they enter the atmosphere.

Primary pollutants enter the atmosphere directly from a natural or artificial source. Thus, car exhaust gases contain carbon monoxide, carbon dioxide and some more complex organic compounds as main primary pollutants. Secondary pollutants are formed due to chemical or photochemical reactions in the atmosphere. These are represented by

Various products of oxidation such as ketons, aldehydes, nitrites, sulfites, ozone and other.

According to duration of their effect, the pollutants in the atmosphere are separated into transient, locally effective pollutants, which do not reach more than 100 kilometers from their source and those with long term effects which are apparent in changes of the composition of the air in large areas and even in disturbances of global conditions. The life of a pollutant in the atmosphere depends very much upon the nature of its source, meteorological conditions and the mechanisms of its disposal from the atmosphere.

The main routes for disposal in the troposphere are chemical reactions, washing out by precipitation and gravitational settling. In the stratosphere the life of pollutants is considerably longer because there are fewer possibilities for disposal and the photochemical reactions are most important.

Sources of pollutants may be either natural or artificial. Though natural sources generate more of the atmospheric pollutants they are of less consequence to humans because they are distributed over the whole surface of the earth. Furthermore, natural pollutants have participated for millenia in natural processes and life on earth is adapted to such conditions.

Artificial pollutants started to influence the composition of the atmosphere only in recent times. Sources of such pollutants are concentrated in narrow regions which are, in addition, also densely populated. Consequently, a large part of the population is directly exposed to their damaging effects.

A Program for Environment (U.N. Environment Programme, UNEP) with defined objective was founded at the Conference of the United Nations on Human Environment in June 1972 in Stockholm. The first task is an evaluation of the quality of the environment, the, so called, "Earthwatch" (5). This task includes measurements of pollutants in the atmosphere and related examinations, such as critical evaluation of data and exchange of information. Within this framework an international meeting was held in 1974 in Nairobi where a priority list of major pollutants was prepared. Air pollutants were listed according to their degree of harmfulness as follows:

1. sulfur dioxide and suspended particulates
2. ozone
3. nitrogen oxides NO and NO₂
4. lead and carbon dioxide
5. carbon monoxide
6. azbestos
7. reactive hydrocarbons i.e. hydrocarbons other than methane

Sulfur dioxide and suspended particulates

90% of the pollutants mass is represented by gases and aerosols represent only 10%. One half of aerosols enters the atmosphere directly as dust, ^{as} sprayed sea foam or as waste from industrial processes. The other half is formed in the atmosphere itself as a product of a series of chemical reactions. A large part of solid suspended particles enters the atmosphere as a product of burning, similar to sulfur dioxide. In this way, two types of pollutants are often regarded as one.

Sulfur dioxide and smoke are long known as atmospheric pollutants. Most drastic examples are related to black London fog, the so called smog. The name smog is derived from the English word "smoke" for smoke and "fog" for fog, which are two primary causes of appearance of a suffocating and dark fog. In recent times the meaning of this word has been broadened to include other types of fogs caused by pollutants. /page 248

Air pollution in London was noticed more than three centuries ago. In 1661 John Evelyn, in his Fumigumium, assigned the cause of high mortality of children, up to 2 years old, to air pollution(6). This type of pollution appears in

relatively cold weather and at high relative humidity. This pollution is caused mainly by burning of coal and fossil fuels (containing a high level of sulfur) in power plants and in homes. Air, polluted by sulfur dioxide, acts upon breathing routes and causes bronchial difficulties. Long exposure to such conditions may cause death, particularly in sensitive persons. Thus, the death of about 4000 people that ^{occurred in London} ~~occurred~~ in a week in 1952 is attributed to a dense smog. Such pollution appears, to a smaller degree at other places such as in the valley of the river Meuse (Belgium), near Pittsburgh and in New-York (USA), in the valley of the river Ruhr (Germany), in Rotterdam (Netherland), Osaka (Japan) and other.

It is certain that smoke and sulfur dioxide have harmful effects on human health even in smaller concentrations. It was thus found in New York that there are 10 to 20 more instances of death when volume concentration of SO_2 is above 0.4 ppm (parts per million) than when it is below 0.2 ppm (7).

The tragedy of 1952 in London has prompted the British Parliament to form a committee to investigate methods by which similar occurrences could be prevented. By use of very tough regulations, the so called Clean Air Act, which forbids ^{burning} ~~burning~~ ^{of coal} ~~in London~~, ^{new tragedies of this type were} successfully averted. The consequence of these regulations resulted in ^a significant reduction of ^{the} concentration of particulates in the atmosphere, and was accompanied by a somewhat smaller change in ^{the} ~~concentration~~ ⁱ of SO_2 .

On basis of analysis of published data on harmful effects of SO_2 and suspended particles, the values given below were proposed by the World Health Organization (WHO) as maximum allowed emissions or concentrations of pollutants ^{to} in the atmosphere. These values are proposed as objectives for air quality (8).

	yearly average	98% days below
SO_2	$60 \mu\text{g m}^{-3}$ (0,02 ppm)	$200 \mu\text{g m}^{-3}$ (0,08 ppm)
smoke	$40 \mu\text{g m}^{-3}$	$120 \mu\text{g m}^{-3}$

In Zagreb, regular determinations of concentrations of sulfur dioxide and smoke (9) have been taken since 1963. These values by far exceed the proposed maximums, as well as the limiting values of other countries (10). Thus, average yearly volume proportions of SO_2 were found to range from 0.03 to over 0.15 ppm. The highest monthly average of 0.24 was recorded in January 1954 (9). Such high concentrations are exceptional even for world proportions. Increased mortality was already noticed at concentrations ⁱ exceeding 0.2 ppm. It is true though, that during the above mentioned episode of pollution in London in 1952, the average volume proportions of SO_2 were 1.34 ppm for duration of two days (11). Average yearly concentrations of smoke in Zagreb are also above recommended standards and are found to be between 50 and $180 \mu\text{g m}^{-3}$. During the winter months the air in Zagreb is particularly heavily loaded with smog of the so called London type. Unfortunately, correlations with any number of death incidents are not known.

Photochemical smog

In the USA, air pollution is most apparent in the city of Los Angeles in California. Some natural fog formation is favored there by its climatic conditions i.e. frequent temperature inversions and configurations of the ground. Back in 1542 when J.R. Cabrillo discovered that country he named the gulph at Los Angeles "Bahia de los humos" (gulph of smoke) (12,13). Even before the Second World War it was observed that pollution in Los Angeles is of a different type than that of London. While the population of London complained about their bronchial difficulties, the main effect of pollution in Los Angeles was eye irritation. The first steps to control further polluting were undertaken in 1947. The first result was a reduction of the amount of dust in the air and thus, an increase in visibility. However, the main symptoms of pollution - eye irritation and harm to plants - were not removed. An investigation of the nature of pollutants was then undertaken. It was found that unlike in London where the air has reducing action due to large concentrations of SO_2 , the polluted air in Los Angeles has oxidizing properties. **Warning** effects of this type of pollution can be attributed mainly to the presence of ozone, peroxyacetylnitrate ($\text{CH}_3\text{CO}_2\text{ONO}_2$, PAN), various organic peroxydes and aldehydes and nitrogen oxides. First effects at low concentrations are observed on plants. Some particular plants such as tomatoes, tabacco, beans etc. show leaf damage even at relatively low proportions of ozone or PAN in the air (12, 13). Plant damage in USA, due to photochemical smog, is estimated to exceed 500 million dollars per year.

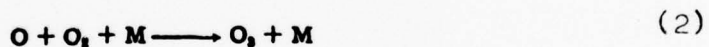
attributed

While there are no known instances of death that can be attributed to photochemical smog, it has been observed (aside from the already mentioned eye and mucous membrane irritation) that **athletes** have reduced strength and that asthmatics **have** increased frequency of attacks. As a standard of air quality, USA allows one hour average maximum of 0.08 ppm of ozone (15) which must not be exceeded more than once a year. The World Health Organization recommends the value of 0.06 ppm as the maximum that should not be exceeded (8). Besides ozone, main oxidants are nitrogen oxides and organic peroxides.

Ozone is a natural component of the atmosphere. Under shortwave ultraviolet radiation in the stratosphere oxygen dissociates into its atoms:



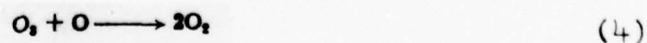
These reactive atoms form ozone in tri-molecular collisions with molecules of oxygen:



where M represents a molecule of air (usually N_2 or O_2), which takes away excess energy. Ozone absorbs ultraviolet radiation very strongly and thus this radiation does not at all penetrate into the lower troposphere. Under influence of sun radiation ozone also photodissociates:



Ozone also decomposes upon collision with atomic oxygen:



According to Chapman (16) the atmosphere establishes a certain equilibrium and a relatively stable distribution of volume ~~proportions~~ ^{concentrations} along altitudes. Chemical reactions, particularly those with radicals such as NO_x , ClO_x and HO_x ($x = 1, 2$), are essential for ^{the} final equilibrium and distribution. A typical profile for the Northern Hemisphere is shown in fig. 3 (17). The volume ~~proportion~~ ^{concentration} of ozone is at a maximum at the altitude of 35 km., where it has a value of 10 ppm. Because of its composition this layer of the atmosphere is also called ozonosphere. This layer acts as a protective filter which protects the surface of the earth from harmful uv- radiation.

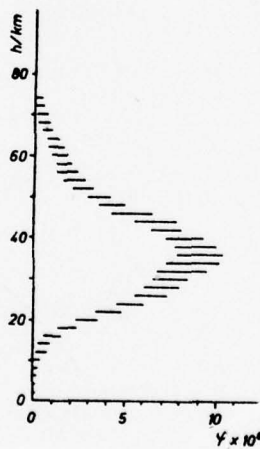


Fig. 3. - Profile of the volume ~~proportion~~ ^{concentration} of ozone (4) as a function of the altitude (17).

Ozone moves from the stratosphere into the troposphere by diffusion and by the vertical ^{currents} exchange of air. Thus, ^{at} the earth surface the concentration of ozone during one hour varies between 0.01 and 0.05 ppm (18). More recently, ^{it was} ~~has~~ ^{by} proposed that a major part of the tropospheric ozone forms by fotochemical processes within the troposphere (19, 20). This theory has not, as yet, been accepted (21, 22).

During times of high pollution levels in Los Angeles the volume concentrations of ozone amounted to over 0.5 ppm. This corresponds to about 1000 tons of ozone in the area of the city. As there is no industry ^{emitting} ~~emitting~~ significant amounts of ozone into the air and temperature inversion prevents any vertical ^{currents} air, the only source of ozone in the polluted city air could be chemical and photo-chemical reactions.

← Radiation that penetrates into this layer of the atmosphere has wavelegths in excees of 310 nm and thus the only absorbing compounds that could be considered are SO_2 and NO_2 . In an oxidizing environment the NO_2 is more important because it absorbs radiation up to 450 nm. Using chamber experiments Haagen-Smit and coworkers have been first to succeed in demonstrating that ozone is indeed formed as a consequence of photo-dissociation of NO_2 in presence of hydrocarbons (23, 24). This type of pollution is therefore refered to as ^{+he} photo-chemical smog or shortly photo-smog. In comparison with the London smog the photo-smog is formed in sunny wheater and at a low relative humidity. Appearance of mist i.e. aerosols is a result of a

large number of chemical reactions that are not at this time completely understood. The brownish color of this smog is caused by presence of NO_2 .

It was long believed that photo-chemical smog appears only in sunny California. However, measurements during the seventies have shown that periods of photochemical pollution can be expected also in more northern regions. Thus, high concentrations of oxidants have been found in Edmonton (25), Ottawa (26), Montreal (27), South England (28, 29), Tokyo (30), Sydney (31), Aspendale (32), Bonn (33), Frankfurt (34) and many other cities.

First ^{ea} measurements in Zagreb have been carried out in summer of 1975, in the very center of the city (35, 36). In the period between May 1st and September 30th, 1975, the American limit for air quality (0.08 ppm) was exceeded for 41 days i.e. for a total of 191 hours. The limits set by the World Health Organization were exceeded during 741 hours. Consequently, one may expect during summer even in our environment some periods of intensive photo-chemical pollution. It is apparent that these problems should be given considerably increased attention.

Carbon monoxide and dioxide

Carbon oxides are primary man made pollutants which are formed almost exclusively by burning of organic fuels. According to the amounts of gases emitted into the atmosphere, these two pollutants are by far the largest.

Even at the ^{beginning} beginning of the fifties it was calculated that human activities emit yearly about 2×10^8 tons of CO into the atmosphere. 85% of that amount comes from car exhausts.

^{The} basic biological sources of CO were not known at that time and thus the volume ~~proportions~~ ^{concentrations} determined to be 0.1 ppm led to the conclusion that the residence time of CO in the troposphere must be 2 to 3 years. This pointed ~~further~~ ^{also} to a possible accumulation of CO in the atmosphere. In the search for a ~~flow-out~~ ^{disposal} mechanism for CO from the atmosphere, it was discovered that the oceans do not represent ~~an outflow~~ ^{a disposal} but a rather a natural source of CO (37). The amount of CO released from the oceans in the Northern Hemisphere is about equal to that released by human activities. In the Southern Hemisphere the oceans represent a significantly larger ^f source. Even larger amounts of CO are formed in the atmosphere by oxidation of methane via free radicals (38). Consequently it is now considered that man made sources generate altogether 10% of the total amount of CO in the atmosphere. Emission of large quantities ^{in comparison} ~~with respect to its~~ ^{the} volume ~~proportions~~ ^{concentrations} in the atmosphere point to existence of a relatively efficient ~~outflow~~ ^{disposal} system. The main outflow for carbon monoxide (39) ^{from the atmosphere} are molds in the ground and higher plants. In addition, part of the carbon monoxide is decomposed in the lower atmosphere.

In cities, particularly in ^{the} dense traffic ~~in the~~ ^{of} city centers, the volume ~~proportions~~ ^{concentrations} of CO can be more than three orders of magnitudes above global concentrations.

In closed premises, such as tunnels, garages and premises with improper heating, concentration of CO can be still higher ^{can} and sometimes even be lethal (above 0.1%).

Carbon monoxide is very poisonous because when inhaled it combines with hemoglobin in blood forming carboxyhemoglobin. This prevents supply of oxygen to the organism. Concentration of the carboxyhemoglobin in blood is directly dependent upon the concentration of the CO in the air. ^{The} Natural concentration of carboxyhemoglobin in blood is 0.8 % (by weight) while for smokers it may exceed 10%. Prolonged concentration of above 4% starts causing first difficulties in humans (tiredness, headache, dizziness). This concentration of carboxyhemoglobin corresponds to ^{re} continued inhalation of air with volume concentration of 25 ppm or to ^{an} one hour exposure to air containing 100 ppm of CO. According to WHO, concentrations in excess of these quantities represent additional risks, particularly for persons with heart diseases (8).

After nitrogen, oxygen and argon, carbon dioxide is the most abundant component of the atmosphere, and it is not poisonous. In spite of that, it is felt that it should receive more attention as a pollutant. Fig. 4 shows how in recent years volume concentration of CO₂ ^{which} continuously rises in various regions ~~that~~ are far removed from influences of civilization (40). These concentrations and an increase of about 1 ppm per year may be regarded as global characteristics.

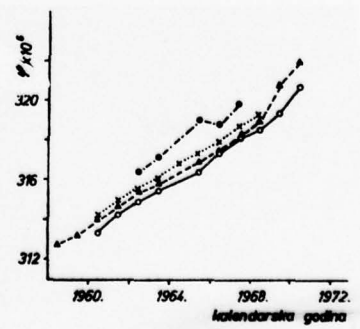


Fig. 4. - /2/ calendar year concentrations of CO₂ (φ) in different regions: ... Alaska; x . ? x Northern Atlantic; ▲ — ▲ Hawaii; ○ — ○ Antarctic (40)

The natural cycle of CO_2 is not completely understood. It is estimated that about 150×10^9 tons of CO_2 is used up yearly for photosynthesis. A large and not clearly determined amount is absorbed by the oceans. The influence of *human* activities on natural equilibrium is not exactly known. However, the above mentioned rise in CO_2 concentration is attributed directly to human activities. It is believed that from the beginning of industrialization, the volume concentration of CO_2 in the atmosphere rose by about 10%, and in recent years this rise has accelerated (41).

Presence of carbon dioxide, along with moisture, in the atmosphere is essential for prevention of cooling of the surface of the earth. Increase in amounts of CO_2 in the atmosphere is thus related to increases in temperatures. Even a small increase in the average yearly temperature would cause partial melting of the polar ice and a significant increase in ^{the} sea level. On the other side, it could lead to changes in currents in the atmosphere and in cloud formation which could have the opposite effect, (42). The degree to which this danger may be real is hard to estimate. The model which is used most often (43) predicts that assuming a constant (present) amount of clouds, doubling of the volume concentration of CO_2 from 300 to 600 ppm would result in a temperature rise of 2°C in the troposphere. At the present rate of temperature rise this would require 300 years. This is certainly not critical for human life but could have great economical consequences. Because many parameters of the model are uncertain the above effects could be significantly greater or smaller.

The major processes should therefore be known more precisely in order to enable timely measures that could avert eventual catastrophic consequences.

PROCESSES IN THE TROPOSPHERE

Abatement of pollution requires an understanding of all factors that influence its formation. This means that it is necessary to be acquainted with chemical mechanisms of smog formation as well as ^{weather} conditions ^{and} climatic factors. Therefore, investigations of so complex a problem include keeping track of concentrations of individual components in polluted air i.e. monitoring, determining changes in pollutants and their residence time in the atmosphere and follow with studies of chemical and photochemical reactions by experimental and mathematical simulation of atmospheric processes.

Methods of measurements used for monitoring of concentrations of individual air pollutants have, in recent years, undergone fast developments. Ten years ago all the methods relied mainly on use of ^{the} classical analytical chemistry. For example, ozone used to be determined by passing a stream of air through a solution of potassium iodide and determining the amount of liberated iodine by titration. Such methods are often sufficiently sensitive and reliable but require very long time and are not adaptable for automation. Methods based on physico-chemical properties of pollutants are therefore much more convenient. Thus, for example, volume concentration of ozone can be determined on basis of its chemoluminescent reaction with ethane as it is used for continuous monitoring of ozone in Zagreb (35). Such methods

R Concentrations of a have regularly better sensitivity and accuracy.
 majority of essential pollutants (CO, CO₂, NO, NO₂,
 SO₂, H₂S, O₃, oxidants, CH₄, reactive hydrocarbons, aerosols
 etc.) can today be automatically monitored, which enabled a
 much faster and more comprehensive regional and global
 collection of data. Global changes in ^{the} composition of the
 atmosphere effect ^{the} global climate and ^{such} ~~their~~ monitoring
 is therefore of interest to meteorology. World Meteorological
 Organization (WMO) has therefore formed a system for tracking
 the weather (World Weather Watch) which collects the data
 on composition of the atmosphere all over the globe (44).

Continuous monitoring of pollutants in densely populated
 areas with considerable industry is necessary ^{simply} ~~just~~ for
 immediate protection of the population. However, it also
 provides information on dependence of pollution upon all /page 251
 kinds of possible factors. Concentration of various pollutants
 in cities have a characteristic time factor, which depends
 upon ^{the} source of pollutants, weather conditions and presence
 of other pollutants. Fig. 5 shows typical daily variations
 of volume concentrations (φ) of some pollutants during
 photochemical smog in Los Angeles (45). It is apparent here
 that high concentrations of ozone occur only with low
 concentrations of NO and during intensive radiation i.e.
 at about noon. A similar daily variation of volume concentrations
 of ozone at the center of Zagreb was shown previously (35, 36).
 Besides daily changes in concentrations it ^{also} is important
 to monitor long term developments in pollution. Thus, for
 example, while volume concentrations of oxidants in Los Angeles

reach very high values, the long term data indicate a decreasing trend. An opposite situation has been found in Eastern American and European cities. Here, maximum hourly averages seldom exceed 200 ppm, but an increase during recent years is apparent. (46). In our country, only smoke and SO_2 have been continuously monitored for a number of years.

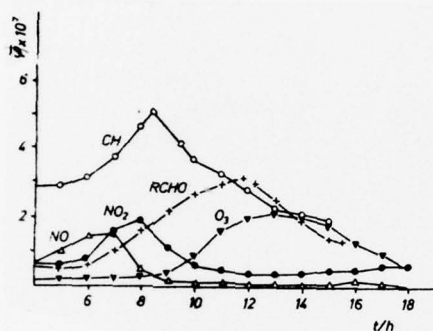


Fig. 5. Variations of daily average volume concentrations proportions (ϕ) of some pollutants in Los Angeles

the photochemical smog of as a function of time. ⁴⁵

The residence time of pollutants in the atmosphere depends upon their reactivity and weather conditions. Chemically inert compounds may stay in the atmosphere very long i.e. for years, while reactive compounds may disappear in a very short time (less than a second). Concentration of primary pollutants is necessarily highest in the vicinity of their source. Secondary pollutants are, however, formed after a while from the primary ones. Therefore, in presence of a wind, maximum concentrations of the secondary pollutants are often significantly removed from the pollution source. A nice example of above was shown

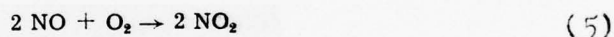
by Georgii and coworkers (47) who measured, from an airplane, the distribution of the concentration of ozone in the valley of the river Rhein, south of Koeln and Bonn. They found the concentrations of ozone near the petroleum refineries and city centers to be lower than those 100 kilometers farther downwind. Similar observations were also made in America (48, 49, 50). This shows that air masses in their movements remain relatively compact and that chemical reactions take place in a manner similar to that of closed vessels. Under such conditions, the effects of ^{the}dillution are smaller. Cox and coworkers (51) have shown that high concentrations of ozone in rural regions of southern England are caused by arrival of air masses from the European Continent, i.e. a few hundereds kilometers away. In such relatively non polluted regions, residence time of ozone in the atmosphere is 1-2 days. High concentrations of sulfur dioxide in southern Sweden are also partially attributed to sources in industrialized regions of central Europe.

Chemical reactions of pollutants are best studied in chambers where under tightly controlled conditions one can vary chemical and physical factors i.e. reactants, their concentrations, intensity of radiation, temperature and other. Similar chambers may be used for studies of biological consequences of pollution. The size and furnishings of such chambers may vary. However, they usually represent a space of a few cubic meters which can, when necessary, be evacuated. Sunlight is usually imitated by use of fluorescent light. These experiments

provide a direct insight into essential processes and mechanisms which determine chemistry in free atmosphere, though they are often far removed from natural conditions. As an example of such investigations, one may describe studies of the photochemical formation of smog.

The sunlight has almost no chemical effect on pure air. Only CO_2 and H_2O absorb radiation in the infrared region. This leads to warming up of the atmosphere. O_2 absorbs very weakly in wavelengths between 750 nm and 1.27 μm , forming very small concentrations of ^{the} electronically excited singlet states.

Even when only nitrogen oxides are added to the pure air a number of reactions become possible. In the atmosphere, NO is formed either from ^{the} natural N_2O , by photolysis, or by oxidation of oxygen at high temperatures, as in motors with internal combustion. In that case NO_2 is formed in a trimolecular exothermic reaction with oxygen:



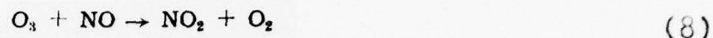
This reaction takes place in ^{the} vicinity of the NO source where its concentration is still high. Of these molecule only NO_2 has strong absorption for sunlight radiation. At wavelengths below 360 nm, photodissociation takes place with its quantum value approaching 1 :



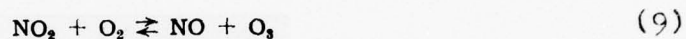
Thus the atoms of oxygen, formed in this process, react mainly with molecular oxygen forming ozone:



Though this is a trimolecular reaction it represents the main reaction path for oxygen due to its high concentration. The resulting ozone reacts further with NO to form again NO₂:



Thus, in absence of other impurities an equilibrium



is established where intensity of radiation and the ratio between NO₂ and NO determines the concentration of ozone. /page 252

If initial volume proportions of NO₂ and NO are 0.050 ppm, (of radiation) after two minutes an equilibrium will be established where

$$\phi(NO_2) = 0.038 \text{ ppm}, \quad \phi(NO) = 0.062 \text{ ppm} \text{ and } \phi(O_3) = 0.012 \text{ ppm}$$

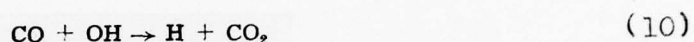
(51). In absence of other impurities, other reactions of nitrogen oxides, ozone and atomic oxygen are negligible. In the presence of moisture there occurs formation of nitrous acid (HNO₂) and nitric acid (HNO₃) which undergo photolysis, when exposed to radiation of the sun, forming very reactive OH radicals (which are however, stable in oxygen). These radicals therefore, react with impurities of the polluted air. When exposed to one hour of radiation an initial volume concentration of $\phi(NO) =$

$\phi(NO_2) = 0.050$ ppm and relative humidity of 50% forms the following volume concentrations of ~~essential~~ ^{major} components:

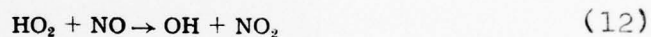
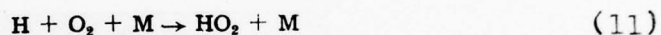
$$\phi(NO_2) = 0.027 \text{ ppm}, \quad \phi(NO) = 0.052 \text{ ppm}, \quad \phi(O_3) = 0.009 \text{ ppm},$$

$\phi(HNO_2) = 0.003$ ppm and $\phi(HNO_3) = 0.008$ ppm (51). In addition, traces of H₂O₂ are also formed leading to formation of HO₂- radical and there is further oxidation of NO to NO₂.

Each additional component increases the number of possible reactions. It was believed that one of the major pollutants - CO - is not reactive in the atmosphere. However, experiments in chambers at high concentrations of CO have shown that this gas has a significant effect on the rate of oxidation of NO in NO, NO₂ and H₂O systems when exposed to radiation (45). CO reacts with OH- radicals according to equation :



which represents a fast reaction and OH- radicals are thus consumed mainly by this reaction (54). Further reactions take place in a chain



which demonstrate a mechanism by which a single OH- radical can cause oxidation of many NO molecules (55). Yet the effect of CO on formation of the photochemical smog in a real atmosphere is considerably smaller (56) because its concentration is lower and because the rate of reaction of OH with olefins exceeds considerably its rate of reaction with CO.

Hydrocarbons present in the atmosphere have a key role in formation of the photochemical smog. Their composition in a city atmosphere varies considerably during the course of a day (57). Thus, olefins are used up much faster than saturated hydrocarbons. Because olefins do not absorb the radiation that penetrates into lower levels of the atmosphere

it may be expected that they might have a relatively long life in clean air. However, in the presence of nitrogen oxides many intermediaries are formed, such as O , OH , O_3 , HO_2 etc., which react rapidly with unsaturated hydrocarbons. In the example of the system air + NO + NO_2 + propane (fig. 6) it is apparent that olefins and NO are used up at a faster rate after a certain time period. Development of O_3 starts only after concentration of NO_2 almost reaches its maximum value. Later on the NO_2 disappears forming peroxyacetyl-nitrate (PAN), organic nitrites and nitrates and nitric acid (59).

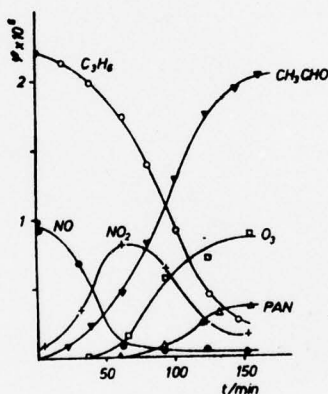
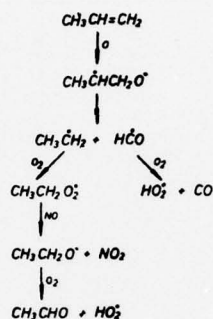


Fig. 6. - Volume concentrations (ϕ) of reaction components in the system Air - NO_x - propane as a function of radiation time (t) (58).

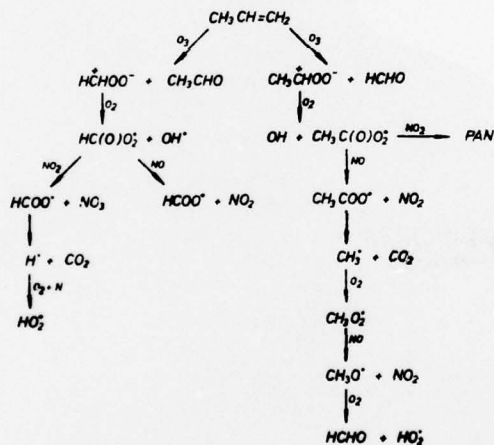
A few mechanisms, varying in complexity, have been proposed to explain photo-oxidation of propane in the presence of nitrogen oxides (58, 60, 51). Simplified schemes I, II and III below illustrate complexity of these reactions. They were used by Niki, Daby and Weinstock for mathematical simulations

of smog formation (58). In such mathematical simulation a certain mechanism is assumed which is converted into a computer program by ^{the} use of interrelated differential equations. In this way

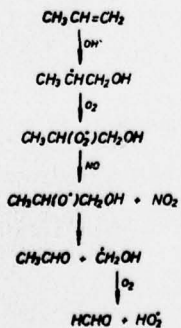
SCHEME I



SCHEME II



SCHEME III



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concentrations of all reactants and products can be calculated as a function of time. Niki and coworkers have considered 150 basic processes and finally selected 60 for purposes of calculations. The resulting agreement with experimental data is shown in fig. 7. A most detailed mechanism using over 200 basic processes was proposed by Demerjian, Kerr and Calvert (51).

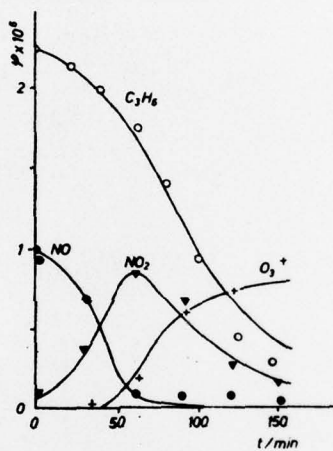
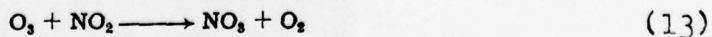


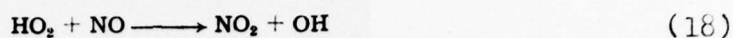
Fig. 7. - A comparison of calculated (~~solid~~ ^{solid} lines) and experimental results (points) for radiation of the system Air + NO_x + propane (58).

Such mathematical simulations of changes of reactants and products with time enable verification of proposed mechanisms of smog formation. At this time, however, reaction kinetics for too many processes is not known. Many constants for reaction rates must be assumed or roughly estimated. Consequently, the resulting agreement with experiments does not mean that a correct mechanism was assumed. It is apparent that such calculations

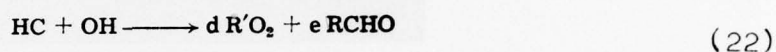
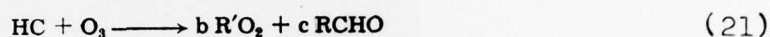
require accurate **data** of kinetic parameters for many reactions. Only relatively few reactions have been, so far, strictly critically evaluated (61). A working group has been founded within CODATA committee which is concerned directly with studies of kinetics of reactions that are **important** for atmospheric chemistry. Consequently the present situation will soon be improved. By studying in detail various basic processes, it will be possible to replace many so far varying parameters with known constants. The mathematical simulation of experiments in chambers will therefore become in the future much more reliable. The advantages of such programs are capabilities to study importance of various processes and components for the total course of reactions and to determine influence of new pollutants.

A simplified mechanism for simulation of reactions in mixtures of hydrocarbons (as found in the exhaust gases of automobiles) can be proposed on basis of importance of individual processes. Hecht and Seinfeld (60) have thus selected 15 reactions out of a complex mechanism of 81 processes and obtained good qualitative agreement with experiments on photooxidation of propane, isobutane, n-butane and mixtures of propane and n-butane. The reactions listed below have been selected in addition to reactions (6), (7) and (8).

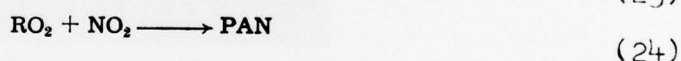
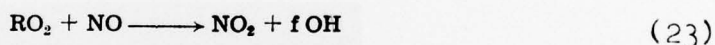




Among the reactions with hydrocarbons (HC), they selected generalized reactions with atomic oxygen, ozone and hydroxy-radicals:



where a, b, c, d and e represent stoichiometric coefficients defined by the composition of the mixture of hydrocarbons (HC). RO_2 represents any of the radicals and often peroxy- and peroxyacyl- radicals. The remaining two reactions describe oxidation of NO to NO_2 and formation of PAN :



where f represents the proportion of OH that was formed from reactions of type (23) i.e. the proportion of the HO_2 -radicals in RO_2 .

In the real atmosphere the processes are far more complex because of effects of other pollutants (such as SO_2 and chlorine compounds) because of heterogeneous reactions on the surface of aerosols and because of dilutions, diffusions, transfer and weather factors. Though such numerous processes and compounds appear a little frightening, they

all together represent the manner in which the troposphere cleans itself from foreign ingredients. The acids that are formed are regularly ~~washed~~ ^{washed} out by precipitation and the composition of the troposphere ~~changes~~ ^{undergoes} considerably slower than it might be expected on basis of the amounts of emitted pollutants.

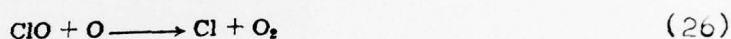
REACTIONS IN THE STRATOSPHERE

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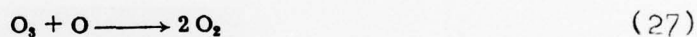
All gases that are emitted from natural and artificial sources do not participate in complex chemical processes of the troposphere. Some of them are very inert, insoluble in water ^{and} non-biodegradable. Their residence time in the atmosphere is therefore considerably longer. Examples of those are freons, very volatile chloro-fluorocarbons among which are most common CF_2Cl_2 and $CFCl_3$. About one million tons of these compounds are produced per year. About 60% of that is used as a pressure gas for spray bottles, 25% is used for refrigeration and the rest for various technical processes. At the start of the seventies, traces of these gases were found above the Atlantic (62). Because these gases are entirely man made it was immediately considered that they should be convenient ~~for~~ for studies of diffusion and transfer processes in the lower atmosphere (63). Volume proportions of 10^{-10} ppm were found in regions far from cities and this is regarded as the global concentration of these compounds.

It was long believed that such inert compounds can not represent any danger to the quality of the environment until Molina and Rowland (64) warned about a new type of danger.

While looking for an outflow mechanism for chloro-fluoromethane from the atmosphere they came to the conclusion that these gases, because of their inertness, remain in the troposphere sufficiently long to diffuse into the upper layers, i.e. the stratosphere. There, at the altitude of 20 to 40 km. they are exposed to the radiation of 175 to 220 nm, in the so called ^{ed} "window" between absorption maxima of oxygen and ozone (fig.1), and photo-dissociate into $CF_2Cl + Cl$ and $CFCl_2 + Cl$. The atoms of chlorine catalyze a series of chain reactions which lead to decomposition of ozone:

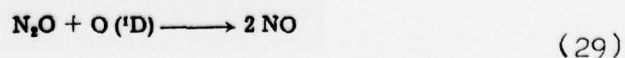
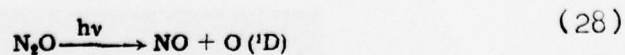


which summarily give :

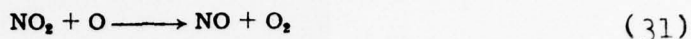


The length of this chain has been estimated to be 10^4 , which means that a single atom of Cl causes decomposition of 10^4 of ozone molecules. Consequently, an increase in concentration of chloro-fluoromethane in the stratosphere can significantly effect the equilibrium of ozone reactions.

Besides the already mentioned Chapman mechanism of photolytic decomposition of ozone in the stratosphere, ozone is also greatly effected by nitrogen oxides. Enormous quantities of N_2O are produced in nature, mainly by bacterial activities. This inert gas penetrates into the stratosphere where it produces NO by photolysis:



Ozone decomposes catalytically also in presence of NO according to the following equations:



Cicerone and coworkers (65) have confirmed, by their mathematical model, that further emission of chloro-fluoromethane could have significant effects on degradation of ozone in the stratosphere (as shown in fig 8.). According to the Chapman mechanism i.e. according to equations (1) to (4) the rate of degradation of ozone is 2.3×10^7 moles per second. Rate of degradation due to nitrogen oxides (NO_x) is somewhat uncertain because neither the amount of NO_x originated in nature nor its vertical distribution are known. Because by far the largest part of the NO_x in the atmosphere originates in nature it can be assumed that this type of ozone degradation will remain constant during the years under consideration. The three curves, denoted as (1), (2) and (3) in fig. 8, represent calculated effects of chloro-fluoromethane for (1) assumption that yearly production of these compounds will continue to grow exponentially as it did from 1960 to 1975; (2) assumption that yearly production of these compounds will remain constant at the level of 1975; and (3) assumption that the production after 1975 is discontinued. It is apparent that even if production of freon were to be discontinued from now on, the degradation of ozone would continue rising for another 20 years. The mathematical models, which include a number of unknown parameters, have brought to attention the danger that in the near future the man made causes of ozone degradation in the stratosphere may exceed those of nature. More recent calculations

show, however, that man made factor at constant level of production should be considerably smaller and be only about 10% of that of nature. (66). Yet even that would have considerable consequences for the life on Earth. Thus, freons are considered a main danger for degradation of the ozone layer. (67).

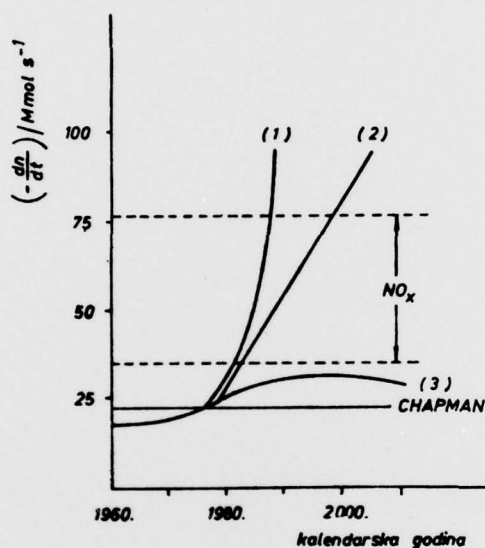


Fig. 8 - /1/ calendar year

- Rate of degradation of ozone ($-dn/dt$) according to calculations by Cicerone and coworkers (65)

Besides the problems of chloro-fluoromethane one should also mention direct pollution of the stratosphere by fast jet planes which fly above the tropopause (68-70). A fleet of ^{just} 500 such planes flying 7 hours per day could double the rate of formation of NO in the stratosphere and thus significantly reduce the amount of ozone.

The consequences of reduction of the concentration of ozone in the atmosphere are still the matter of very crude estimates. The fact is that uv-radiation, which is damaging to life, would penetrate into the troposphere with a significantly higher intensity and thus have direct influence on the biosphere i.e. on plants, animals and people. Cancer of the skin may be taken as an example because its frequency may be readily estimated. It is thus anticipated that just in the USA this ~~disease~~^{ailment} would increase by about 8000 cases per year for every percent of reduction of ozone concentration in the stratosphere. (71). In addition, photochemical activity^{is} in the troposphere would be increased and temperature, structure and dynamics of the stratosphere would be changed. It is even more difficult to foresee further secondary consequences.

At this time, it remains certain that atmosphere does not have an unlimited capacity to absorb chloro-fluorocarbons. Their emission into the atmosphere should be done with considerably more caution until all processes and consequences related to use of these compounds are better known. More recent measurements have shown that the concentration of freon in the atmosphere increases in proportion to world production and that the total quantity present in the troposphere corresponds to the amount produced to date. ((72). Thus, theoretical assumptions of Molina and Rowland (64) and Cicerone and coworkers (57) and Crutzen (73) and others have been confirmed and the problem is becoming more and more critical. Though the biological consequences of^a reduction of the protective ozone layer remain mostly unknown the physico-chemical evidence indicates that emission of freon into the atmosphere must be limited.

The industry is therefore searching for new gases for pressurizing spray cans and some firms in the USA are already using new preparations.

CONCLUSIONS

It must be apparent to the reader of this article that the problems related to the studies of atmosphere pollution are very complex and include a variety of scientific branches from mathematics, geophysics, physical and analytical chemistry to biology, medicine and social sciences (such as law and economy). While many problems have here been omitted it is apparent from what has been presented that considerable fundamental research is needed to improve understanding of all essential processes. Furthermore, the methods of measurements should be improved and an adequate measuring network should be established to assure the necessary living conditions for the future generations. There is need, even in Yugoslavia, to pay more attention to the problems of pollution of the environment, to get included into the world monitoring network and to adequately follow and study processes that take place in the areas of our cities.

ACKNOWLEDGEMENT

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Summary

A review of the more important types of air pollution is presented and mechanisms and factors which effect formation of smog are discussed. Chemical and photo-chemical reactions which take place in the troposphere are described. Particular attention is given to new research of processes which lead to formation of the photo-chemical smog. Degradation of ozone in the stratosphere is also described as a consequence of emission of inert chloro-fluorocarbons into the atmosphere.

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