

SURVEY OF THE DISTRIBUTION OF TRACE SUBSTANCES IN PURE AND POLLUTED ATMOSPHERES

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ABSTRACT

The main reactive air pollutants are SO₂, H₂S, sulphate compounds, NH₃, NO, NO₂ and other oxidants and hydrocarbons. On the basis of a survey on the production and mean distribution of these compounds in pure and polluted atmospheres several chemical reactions are considered. The meteorological parameters, sun radiation, water vapour and the liquid water content of clouds modify these chemical reactions in the atmosphere.

The distribution of trace substances in the atmosphere is a very complex subject. In a survey trace substances may be subdivided according to their importance in air chemistry, hygiene, and meteorological aspects in the troposphere.

HYDROCARBONS IN THE ATMOSPHERE

With chemical reactions in the atmosphere, great emphasis has been laid on hydrocarbons, which are emitted mainly by automobiles (evaporation of fuel, blow by and exhaust). Early analyses of these contaminants are referred to by Magill and Littman in 1953³⁹. The composition of exhaust gases depends on the state of the automobile and on driving conditions (see for example^{43, 47}). In the literature, hydrocarbon concentrations are referred to as carbon-, methane-, hexane-, propane- or ethene-equivalents. The reactivity of hydrocarbons (HC) was studied by Altshuller¹, who defined the reactivity according to product yields and troublesome effects (production of ozone, PAN, formaldehyde, aerosols and the effects of eye irritation and plant damage). On this basis, C₅- and heavier paraffins, olefins and most aromatics are reactive. These conclusions are drawn from bulk analyses of HC.

Stephens⁵³ analysed outdoor air before and after irradiation (UV) for single HC-components. From these measurements *Figure 1* shows the concentration of a number of light hydrocarbons (full line). The dashed line represents the percentage of the HC found after 24 hours irradiation. This percentage is also an indication of reactivity. There seems to be a difference according to whether single HC-components are studied or a mixture of different HC and nitrogen oxides³⁴ as is found in outdoor air. *N*-butane was present (*Figure 1*) in the sample to the extent of 120 ppb and this was found after irradiation to be reduced to 65 per cent = 78 ppb, i.e. 42 ppb had been destroyed. This unreactive *n*-butane from ambient air loses more

HC to photochemical reactions than the reactive 1-butene (6 ppb before irradiation and only 8 per cent = 0.5 ppb recovered).

Nothing is known about the distribution in the atmosphere of most hydrocarbons. Although methane (CH_4) is distributed all over the earth, only rough estimates of its behaviour in the atmosphere have been given⁸⁵.

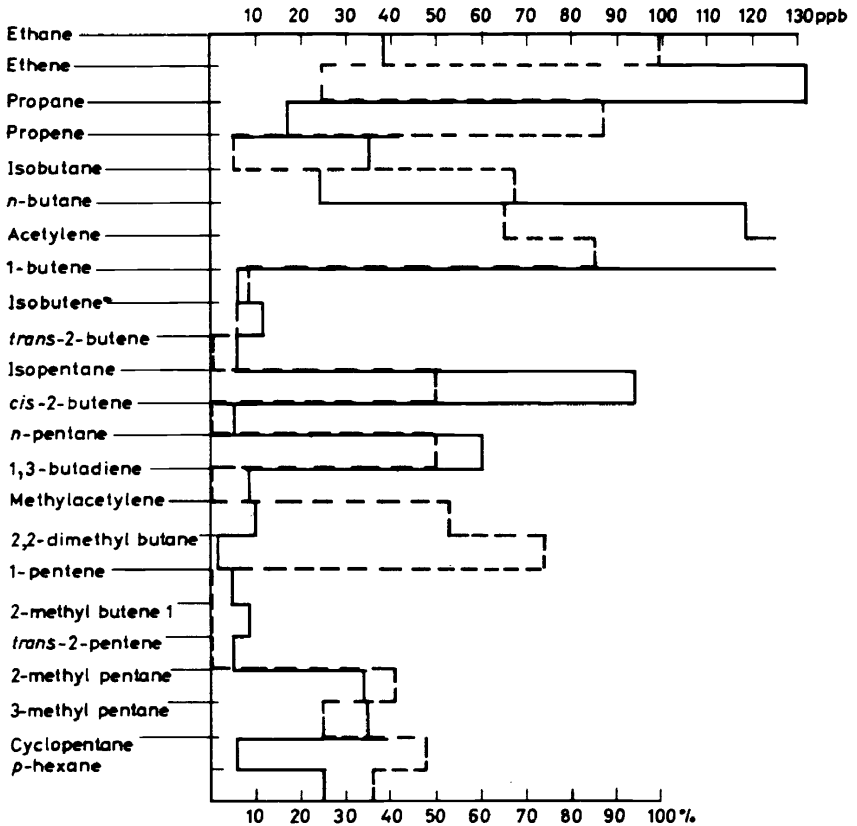


Figure 1. Light hydrocarbons in ambient air and remaining hydrocarbons after irradiation

The lifetime is estimated to be 20 years, based on some known natural CH_4 sources (paddy fields, enteric fermentation of animals, coal fields, upland fields and forests, but not swampy areas) and based on the whole amount of methane in the atmosphere (mean concentration 1.5 ppm). Ehhalt¹⁰ argued that the residence time of methane in the atmosphere must be shorter than 20 years as he measured relatively strong variations in the vertical distribution and at different times. The only sinks of methane known are the consumption by some bacteria, the reaction with O and O_3 and perhaps the adsorption of CH_4 on dust as shown by Liberti⁶². The destruction of CH_4 by oxidation accounts for only 10 per cent of the known production. The C^{14} content in CH_4 probes shows that 75 per cent of methane is of biological origin. Better

estimates of the CH_4 balance in the atmosphere will be possible when the present high level of C^{14} in atmospheric CO_2 is transferred to methane by plants.

The generation of oxidants and plant damaging effect of hydrocarbons described by Haagen-Smit²² led to consideration of the role of HC in air pollution. The prevailing concentrations of single HC-components in outdoor air are unimportant from the hygienic point of view. The mean concentration of total HC is only about 2 ppm C and 97.5 per cent of the concentration frequency distribution in larger American cities registers only about 5 ppm⁶³. Concentrations reported from European cities range 1 to 2 ppm lower (for example⁵²). Cole and Katz⁷ report the transport of HC, oxidant precursors and oxidants over some 100 km. They only found plant damage in humid air masses up to 100 km. from industrial areas.

There are several HC in exhaust gases, which lead to eye irritation without irradiation, e.g. formaldehyde¹, whereas other HC bring this effect after chemical reaction, e.g. *trans*-2-butene mixed with ethylene and irradiated with near UV-light¹. Most reactive HC form eye irritants and oxidants in mixtures with NO and NO_2 ⁵⁰. In these gas mixtures NO_2 absorbs sunlight and yields O which is needed in ozone- and oxidant formation. This O reacts to form NO_2 again, but Tuesday⁵⁷ found that NO_2 formation from NO in outdoor air exceeds NO_2 destruction by a factor of 5. This relation is supported by comparing the diurnal variation of NO, NO_2 and oxidants³⁸. During morning hours, 7 to 8 o'clock local time, the NO concentration has a peak resulting from the traffic rush hour which is followed by a sharp decrease of NO and an increase in NO_2 concentration. Certainly the sum of NO and NO_2 is decreasing after the rush hour due to the decreasing NO production by traffic and also to the increasing atmospheric turbulence. The rates of the main chemical reaction leading to NO_2 in the atmosphere are referred to by Altshuler². Consideration of the chemical equations giving rise to photolytic destruction of NO_2 prove that the NO_2 concentration in outdoor air is too small for the supply of sufficient O atoms for ozone and oxidant formation. In several American cities the oxidant concentration reaches some 200 ppb, while the NO_2 concentration amounts only to 100–150 ppb. Due to this finding Haagen-Smit and Wayne²³ postulate chain reactions producing oxidants in urban air initiated by sunshine. Some of these chain reactions include the formation of peroxyalkyl nitrate (PAN), an oxidant analysed in several American cities and studied by Stephens⁵⁴. The highest oxidant concentrations are reported from Los Angeles where the concentration of air pollutants (very high concentrations of exhaust) and the meteorological situation (intensive and prolonged sunshine, frequent temperature inversions and mixing of polluted air with maritime air) yield photochemical reactions in the atmosphere. As regards the composition of the polluted air Hamming and Dickinson²⁴ found that eye irritation, which is closely correlated with oxidant concentration, depends upon relative concentrations of N-oxides and hydrocarbons in the outdoor air. Assuming 1.0 ppm HC and 0.2 ppm NO_x in ambient air, irradiation (4 h) is followed by eye irritation. Decreasing HC concentration leads first to increasing eye irritation and only a further decrease in HC causes a decrease in eye irritation.

Oxidant concentration, including natural ozone, ranges from 0 to 1 ppm

as measured in Los Angeles. For comparison, in San Francisco the mean oxidant concentration is 50 ppb, in Cincinnati 25 ppb⁵⁸ and Frankfurt 22 ppb⁴¹. The mean natural ozone concentration in middle latitudes is some 20 ppb. Lahmann *et al.*³⁶ found reducing air pollution in Berlin. In streets with heavy traffic the ozone concentration was always low compared with that in rural air. In Frankfurt apparently anthropogeneous oxidants were measured as shown in *Figure 2* by the higher ozone concentration in Frankfurt compared with that measured on the nearby Taunus Observatory (840 m). Also shown are synchronous measured concentrations of NO₂ and HC, wind velocity and sunshine. Natural ozone has its main source in the stratosphere and therefore increases with height. *Figure 2* shows a decrease which points to a source in low levels. During these days the maximum ozone concentration (measured by neutral buffered KJ method) occurred about noon. The peak of natural O₃ usually is found one to three hours later.

The participation of sulphur dioxide (SO₂) in HC consuming reactions supports the aerosol formation of HC. The formation of aerosols from mixtures of reactive HC was discussed (for example^{2, 19}). The participation of SO₂ in this aerosol forming process was experimentally proved e.g. by Endow *et al.*⁶³.

Dust analyses for aromatic HC are reported from De Maio and Corn⁹. In polluted air they found the polynuclear aromatics amounting to some 2 per cent of the total suspended material. Several benzpyrenes, fluoranthene and benz- α -anthracene were analysed. Some of these aromates generate cancer.⁴⁹ Moore *et al.*⁴² found 6–50 μ g 3-4-benzpyrene per 1000 m³ of outdoor air (similar concentrations of fluorethene, 1-2-benzpyrene, 11-12-fluoranthene, 1-12-benzperylene).

In addition to this particulate matter, other studies have been made of aerosols in atmospheric photochemistry for heterogeneous reactions. Aerosols may emit trace gases after irradiation. The desorption of NO_x from nitrate aerosols was studied by Gori *et al.*²⁰ According to these authors ammonium nitrate in aerosols decomposes to H₂O, NO and NO₂. The mechanism of desorption is still unknown; NaCl acts as a promoter in these reactions.

Summarizing the position regarding HC distribution we may say: non-methane hydrocarbons are emitted in urban areas mainly by automobiles. In ambient air the concentration of HC which depends on the traffic situation is harmless from the hygienic point of view (mean 1 to 5 ppm C). Relative HC concentrations in gas mixtures and variation of the concentration are important in the field of air chemistry and hygiene as HC forms severe eye-irritants, oxidants and dangerous aerosols. There are several reactions known of HC groups as well as of single HC components. These reactions include mainly NO_x, SO₂ and NaCl. But until now there has been no possibility of giving a balance of reactions in the atmosphere leading to the observed production and destruction of oxidants. Anthropogeneous oxidants were found in Los Angeles, and in other American cities which are prominent for heavy traffic and high concentrations of HC and nitrogen oxides. Also from Japanese and European cities situations are reported which indicate the presence of large concentrations of oxidants. The aerosols formed by photochemical reactions lead to sight interference and at very high concentrations, which have not yet been reported in ambient air, they generate cancer.

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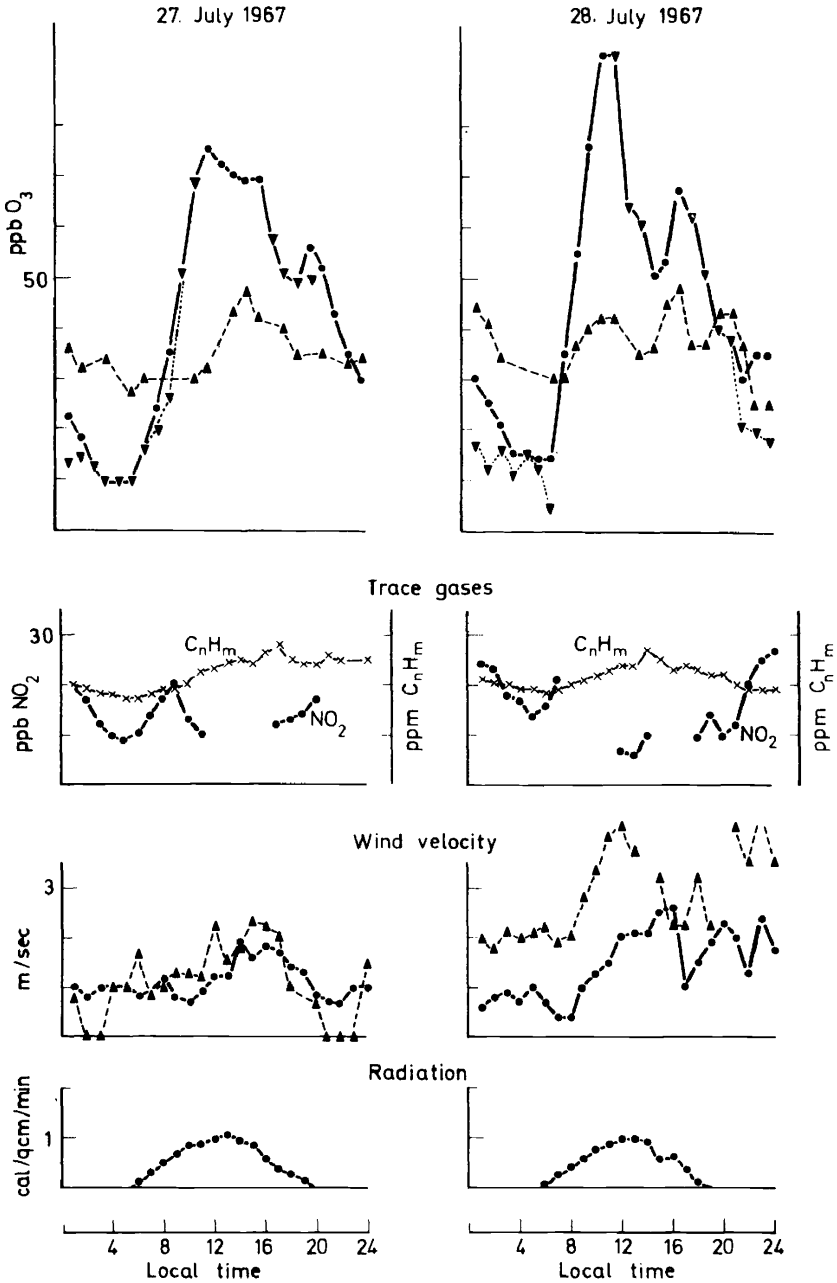


Figure 2. Daily variation of O₃, C_n H_m, wind velocity and sun radiation.

- measured in Frankfurt/Main
- ▲—▲ measured on Taunus Observatory
- ▼—▼ O₃ measured continuously
- ▼...▼ O₃ measured intermittently

Nothing is known concerning middle and large scale distribution of non-methane HC.

SULPHUR DIOXIDE IN THE ATMOSPHERE

A further trace substance common to air chemistry and hygiene, and also to meteorological studies, is SO_2 . This gas reaches high concentrations in industrialized areas during stagnating weather situations. The main anthropogeneous sources of SO_2 include: burning fuels containing up to 3 per cent sulphur¹¹; mining⁴⁸; chemical industries²⁵, and emission from the interior of the earth²⁶. But the most efficient SO_2 source is oxidation of naturally emitted H_2S ¹². SO_2 measurements are reported from all industrialized nations. Until now there exists no economic gas cleaning device for retention of SO_2 from stack effluents. The only way to limit SO_2 concentration is to build tall stacks. The distribution of SO_2 in the lee-side of stacks has been the subject of many technical and meteorological studies (for example^{8, 33}).

The studies are based on SO_2 measurements at ground level around stacks, and on the assumption that the crosswind distribution of SO_2 follows the simple normal distributions. Measurements by Jost²⁸ indicate that in the vertical plane the CO_2 (or SO_2) concentration may not be described by simple normal distributions but by exponential functions or by several superposed normal distributions. The maximum of stack emissions was found at the height of wind maximum. Until now all these measurements on the lee-side of stacks could not yield a complete picture of effluent distribution. Vertical distribution of SO_2 in central Europe was studied by Georgii and Jost¹⁴. SO_2 decreases with height, as is shown in *Figures 3 and 4*. The influence of single industrial areas was found to reach up to about 1000 m whereas the SO_2 concentration was higher than that reported for relatively pure atmosphere for up to 5000 m¹⁵. SO_2 measurements in relatively pure atmospheres were made possible by an analytical method invented by West and Gaeke⁶¹. This method was tested and improved by Lodge³⁷ and Nietruck⁴⁴. Further SO_2 measurements in fairly pure atmospheres are reported^{13, 29, 60} which indicate that the SO_2 concentration amounts to $0.6 \mu\text{g SO}_2/\text{m}^3$ on Mount Corviglia in the Alps, or to $1.1 \mu\text{g SO}_2/\text{m}^3$ on Hawaii, whereas the SO_2 concentration in polluted atmospheres in Europe ranges from about $10 \mu\text{g SO}_2/\text{m}^3$, as a mean during summertime, and up to some $500 \mu\text{g SO}_2/\text{m}^3$, as a mean during wintertime. Recent measurements in the equatorial Atlantic indicate that SO_2 concentration are less than $0.2 \mu\text{g SO}_2/\text{m}^3$ in areas without any industrial influence.

The yearly increase in SO_2 concentration due to anthropogeneous SO_2 production was estimated by Altshuller¹ as $15 \mu\text{g SO}_2/\text{m}^3$. But even in central Europe the SO_2 concentration amounts only to $10 \mu\text{g SO}_2/\text{m}^3$ during summertime. The relatively low SO_2 concentration is due to 'selfcleaning' processes in the atmosphere (e.g. wash-out by rain) and to chemical reactions of SO_2 in the atmosphere.

There is photochemical oxidation of SO_2 to SO_3 which is converted to sulphate in a humid and polluted atmosphere. This oxidation was considered by Rensetti *et al.*⁴⁶, who estimate the oxidation rate as 0.1 to 0.4 per cent per hour. Gerhard and Johnston¹⁸ measured the photochemical oxidation of sulphur dioxide to be independent of humidity, salt and NO_2 content of

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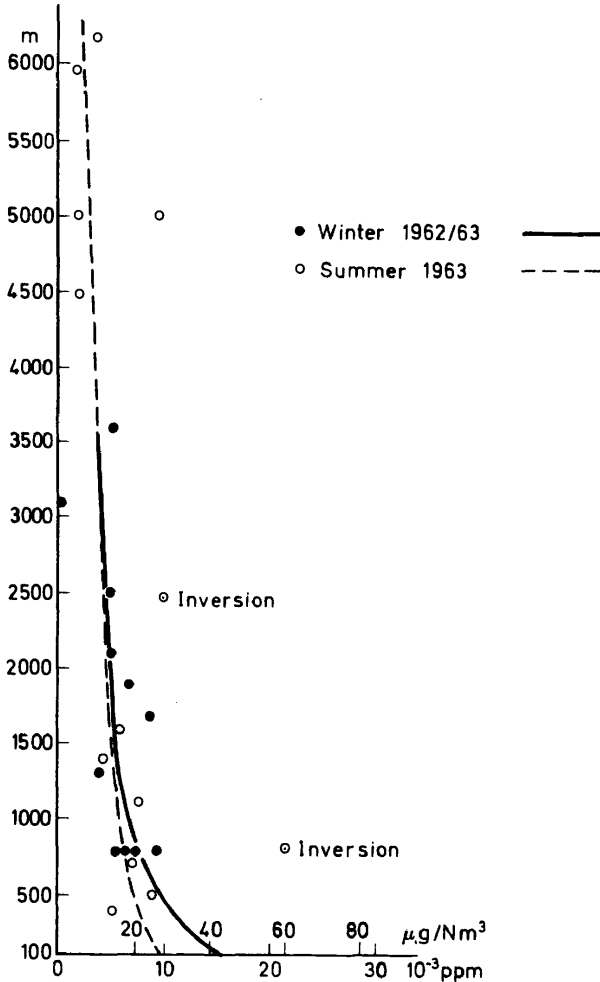


Figure 3. Vertical distribution of SO₂ concentration from aircraft ascents.

the examined gas mixture. Prager *et al.*⁴⁵ studied aerosol formation by irradiation in gas mixtures containing O₃ + olefines, NO₂ and SO₂ and found that SO₂ promotes aerosol formation. Also Gunn²¹ observed that the formation of Aitken-nuclei correlated with the SO₂ concentration. Shirai *et al.*⁵¹ measured SO₂ oxidation as a reaction of the first order being promoted by humidity. A most extensive study on aerosol formation in gaseous mixtures was carried out by Stevenson⁵⁵ with different HC, NO₂, SO₂ and H₂O. SO₂ always promoted aerosol formation. The lifetime of SO₂ in the atmosphere determined by solar radiation amounts to 40 days in middle latitudes³¹. In industrialized regions the lifetime will be shortened as indicated by aerosol formation from HC-NO_x-SO₂ mixtures. Coagulation of these aerosols leads to larger particles which fall out.

Adsorption of active trace gases e.g. SO_2 on the surface of aerosols results in an accumulation. Thus aerosols may build so called hot spots as the SO_2 is possibly oxidized to sulphuric acid after adsorption. This reaction is catalysed by several salts of heavy metals. Liberti⁶² made measurements of the surface area of atmospheric dust particles. He never found SO_2 to be adsorbed and concluded that this compound was oxidized immediately. Carpenter⁶ found from plumes SO_2 decreasing by 3 per cent during 60 minutes after emission when the plume is dry, and by about 28 per cent in a humid plume. Sulphate formation by UV radiation was independent of humidity but the catalysed oxidation of SO_2 is strongly dependent on humidity.

Further SO_2 consuming reactions take place in the liquid phase. Terraglio *et al.*⁵⁶ studied the absorption of SO_2 by water films. They found an equilibrium of SO_2 adsorption and desorption after some 2 hours. With increasing SO_2 concentration in the air the equilibrium concentration in water also increased. With high SO_2 concentrations in the air, saturation of water with SO_2 is reached faster than with lower SO_2 concentrations. Therefore SO_2 adsorption by water is assumed to be a reaction of the first order. SO_2 absorption is gained by acidity. This acidity may be estimated from $\text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_3$ and $\text{H}_2\text{SO}_3 \xrightarrow{K_1} \text{H}^+ + \text{HSO}_3^-$. The catalysed oxidation of sulphur dioxide in solutions of FeCl_2 was studied by Junge and Ryan³⁰. A further important reaction of SO_2 is reported by van den Heuvel and Mason⁵⁹. They found that ammonia regulates the acidity in droplets exposed to SO_2 . Johnstone and Moll²⁷ found that MnSO_4 catalyses SO_2 oxidation in fog droplets. The absorption of SO_2 by droplets and subsequent oxidation is one of the main sinks of SO_2 from the atmosphere. As experiments by Georgii and Beilke¹⁶ indicate that 'selfcleaning' of the atmosphere (washing out by rain) is dependent on meteorological parameters, like droplet concentration and size inside and below clouds, and on the intensity of the rain. The experiments by Georgii and Beilke support the findings in studies of natural rain which show the sulphate content of rain water to be highest during rain falls of low intensity. The SO_2 concentration in a fairly pure atmosphere of central Europe (more than 100 km distant from industrial areas) will not contribute to measurable variations of acidity in open waters.

From SO_2 consuming reactions it is concluded that the lifetime of SO_2 in industrial regions (HC, NH_3 , catalysts, UV, precipitation) will be shorter than in the pure atmosphere (UV, precipitation). This is also supported by SO_2 absorption by soil and plants⁴⁰.

With increasing distance from the source, the lifetime of SO_2 increases. In a pure atmosphere the ratio $\text{SO}_4^{=}/\text{SO}_2$ increases with increasing distance from the source. This is demonstrated in *Figure 5* where the vertical distribution of SO_2 and sulphate from an aircraft ascent is shown¹⁵. In a similar way the ratio $\text{SO}_4^{=}/\text{SO}_2$ may be considered as an air mass indicator with respect to the transport from industrialized regions. As sulphate is the final rate of sulphur in the atmosphere, the sum of SO_2 + sulphate seems to be a good indicator for air mass characteristics. This is seen in *Figure 6* where total sulphur was changing from 2.5 to 5 $\mu\text{g S}/\text{m}^3$ when the air mass in St. Moritz in the Alps changed from subtropical and maritime to a continental type¹⁷.

Growing industries and increasing energy demands lead to increasing

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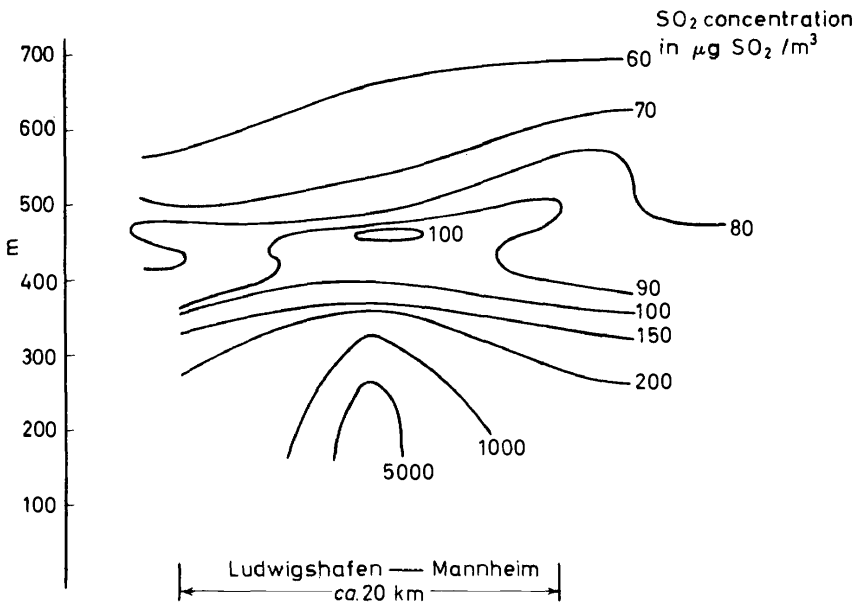


Figure 4. SO₂ concentration over the industrial area Mannheim-Ludwigshafen (3rd April 1965).

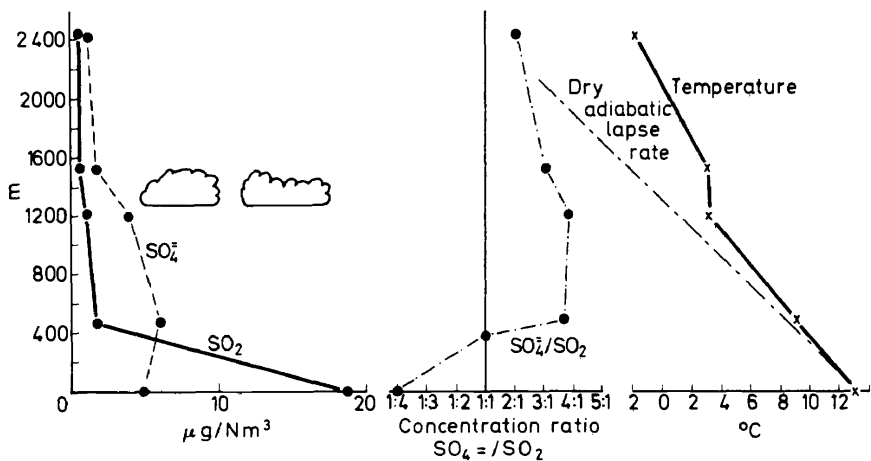


Figure 5. Vertical distribution of the SO₂ and SO₄⁻ concentration (15th March 1967).

CO₂ production by burning organic fuels. Nevertheless photosynthesis and decomposition are the main CO₂ sources and sinks. Whereas natural CO₂ production and consumption have been in equilibrium for centuries, the increasing industrial CO₂ production leads to a rising CO₂ level in the atmosphere since about 1900⁵. Brown and Keeling⁴ report an annual increase

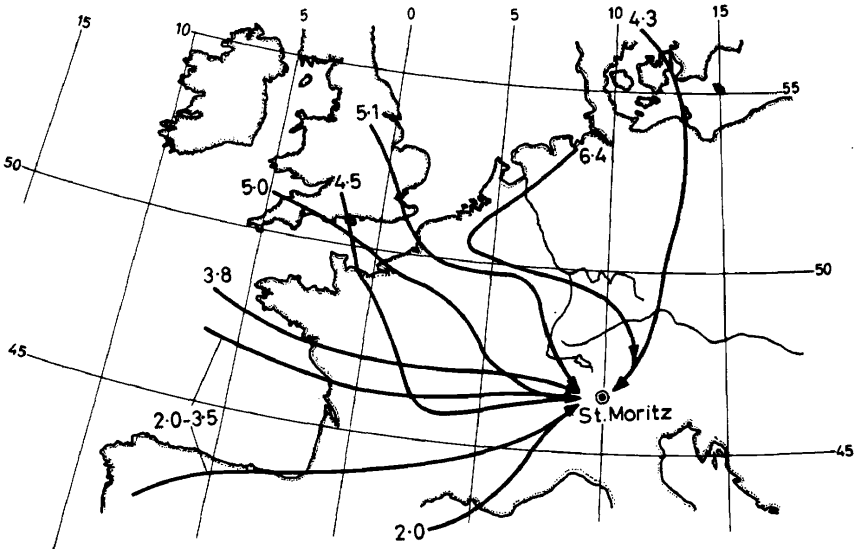


Figure 6. Air masses and sulphur content ($\mu\text{g}/\text{m}^3$) in St. Moritz.

in CO_2 concentration of 0.7 ppm CO_2 per year. Variation of CO_2 concentration is caused by CO_2 production (assimilation and burning) and by atmospheric turbulence. During the late winter a maximum in CO_2 concentration is found and in early autumn this reaches a minimum. This yearly variation has been measured up to heights of 1000 m by Bischoff³. The average CO_2

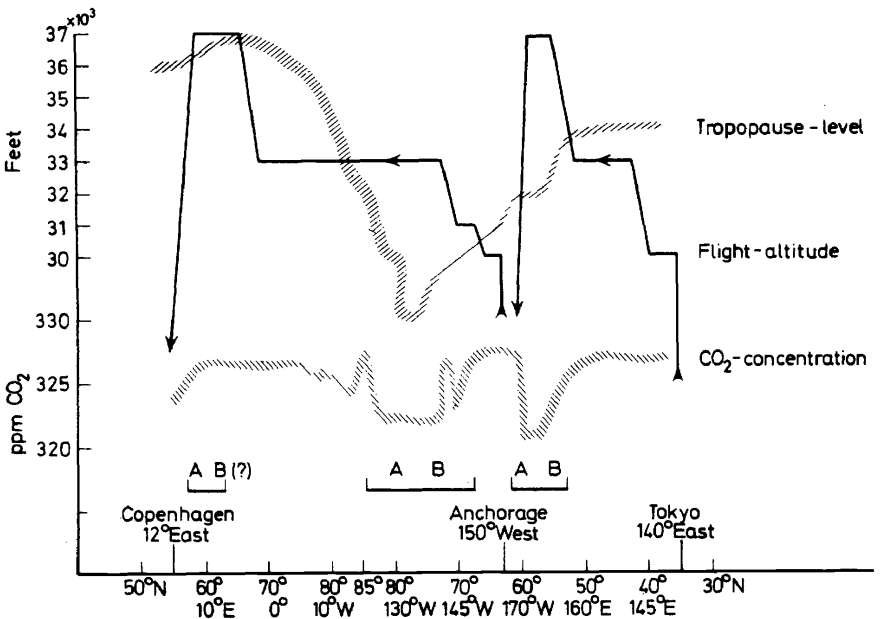


Figure 7. Transpolar flight Tokyo-Frankfurt (29-30th May 1967).

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concentration decreases with increasing height. Measurements by Georgii and Jost¹⁷ show decreasing CO₂ concentrations from the troposphere to the stratosphere (Figure 7). Calculations of CO₂ increase based on estimations of fuel consumption lead to an overestimation of CO₂ concentration. This is due to CO₂ absorption by the oceans lowering the concentration of atmospheric CO₂.

Many chemical reactions in air pollution are not yet well understood. The balance of the pollutants and also their distribution demand more research. The part played by water as a sink of air pollution is still to be studied. As the chemistry of air pollution is generally very complex, CO₂ seems to be a good tracer for studies of the anthropogeneous influence in the balance of atmospheric contaminants.

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