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THE LONG RANGE TRANSPORT OF AIR
POLLUTANTS

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1 INTRODUCTION

Air pollution by man's activities began with the discovery of fire and combustion products still plague the inhabitants of cities, although there has been a shift from the fumes of wood and coal fires towards auto exhaust and photochemical oxidants. Since the middle of this century, it has been realized that combustion products are affecting atmospheric chemistry also outside urban and industrialized areas, but only during the last decade it has become evident that air pollutants may contaminate substantial parts of the global atmosphere. The significance of this contamination of our environment depends on the amounts emitted in relation to the natural background, the chemical persistency of the components, as well as their dispersion and deposition. For some substances with a relatively high vapour pressure, as mercury and many chlorinated hydrocarbons, re-emission to the atmosphere by sublimation is also an important factor.

The continuously increasing population of the world and the tremendous production capacity of modern industry, have given a new dimension to air pollution during this century. The concentration of carbon dioxide has increased from approximately 295 ppm by the turn of the century, to a level of about 340 ppm at present. The haze formed over industrialized areas such as the European continent and the eastern part of North America and the adjoining seas is easily recognized from aircraft and satellite observations (Bolin and Charlson 1976, Lyons 1979), and the long range transport of gases and aerosol particles is now well documented (OECD 1977, WMO 1979).

The clean atmosphere, in addition to its main components nitrogen, oxygen, water and carbon dioxide, also contains highly variable amounts of gaseous and particulate components from wind erosion,

biological activities, forest fires, lightning, volcanic eruptions, etc. By air pollutants we mean substances emitted to the atmosphere by the activities of man. The air is polluted if the concentrations reach levels which may have negative effects on our health, our environment, or materials we use.

Most of our experience with long range transport of air pollutants comes from studies at middle latitudes in the northern hemisphere. An evaluation of other source areas which may contribute significantly to the world wide pollution of the atmosphere has been made by Hidy et al. (1980). The amounts of atmospheric contaminants released by the consumption and combustion of fossil fuels, and the dispersion of certain chemical compounds, makes it necessary to consider seriously the capacity of the atmosphere and our environment to receive these various components without substantial adverse effects. In order to do this, the emission sources, atmospheric transport mechanisms and sinks must be known.

2 THE SOURCES OF AIR POLLUTION

The major emissions of air pollutants are due to the use of fossil fuels for heat and energy production¹⁾, including motorized traffic. In addition come the emissions from industrial production processes which in some areas may be the dominating source, and the large scale use of many industrial products, e.g., fertilizers, solvents, pesticides, freons, etc.

1) Emissions to the atmosphere from nuclear energy production fall outside the scope of this survey.

The growing use of fossil fuels in Europe during this century is illustrated in Figure 1 (Semb, 1978). The early sulphur dioxide emissions in Europe were mainly due to the combustion of sulphur containing coals and in some areas the processing of sulphidic ores. The increased demand for energy after 1950 was met by a wide-spread introduction of petroleum products, and as a result the sulphur dioxide emissions in Europe were doubled in the period 1950-75. Later they have not changed much. On a global scale, industrial processes (mainly roasting of sulphidic copper, nickel, lead and zinc ores, manufacturing of sulphur acid, and the paper and pulp industry) account for about 10% of the total sulphur pollution (Cullis and Hirschler, 1979).

In North America the sulphur dioxide emissions mainly originate from the use of coals with a relatively high sulphur content and from special industries. The relative contribution from oil combustion is much smaller than in Europe. Figure 2 shows the summer and winter coal consumption in USA since 1940 (Husar et al., 1979). It shows a peak in 1943 and since 1960 the summer consumption has grown at a rate of 5.8% p.a. as compared to 2.8% p.a. for the winter. In addition to this, the consumption of heavy fuel oil has increased by 50% since 1959.

In addition to sulphur dioxide, the emissions from industrialized and density populated areas include a large number of other chemical components which are emitted to the atmosphere from many different sources. For practical purposes, one may distinguish between pollutants which occur in such quantities that acute effects may be observed near the sources, and pollutants which appear in smaller amounts, but may give rise to long term effects due to accumulation in the environment, or in the human body.

Well known pollutants in the first group are in addition to sulphur dioxide, the nitrogen oxides, and other aggressive chemicals, such as elementary chlorine, fluorine, and their hydrogen acids. There are also the less specific components consisting of particles and hydrocarbons. In the atmosphere, these components undergo various chemical reactions, and secondary pollutants, such as sulphuric

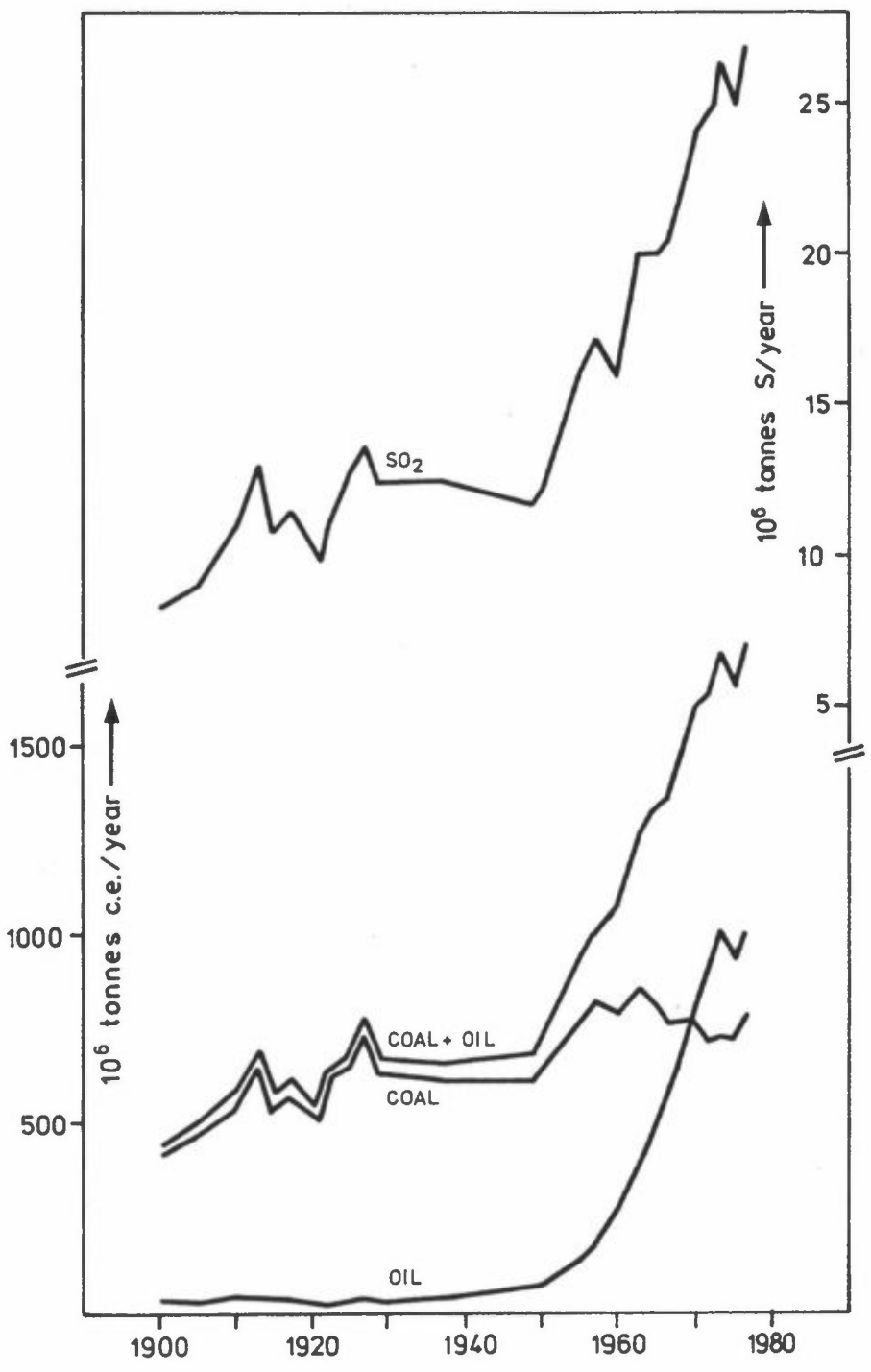


Figure 1 :

Consumption of coal and oil in Europe and estimates of the resulting sulphur dioxide emissions since year 1900.

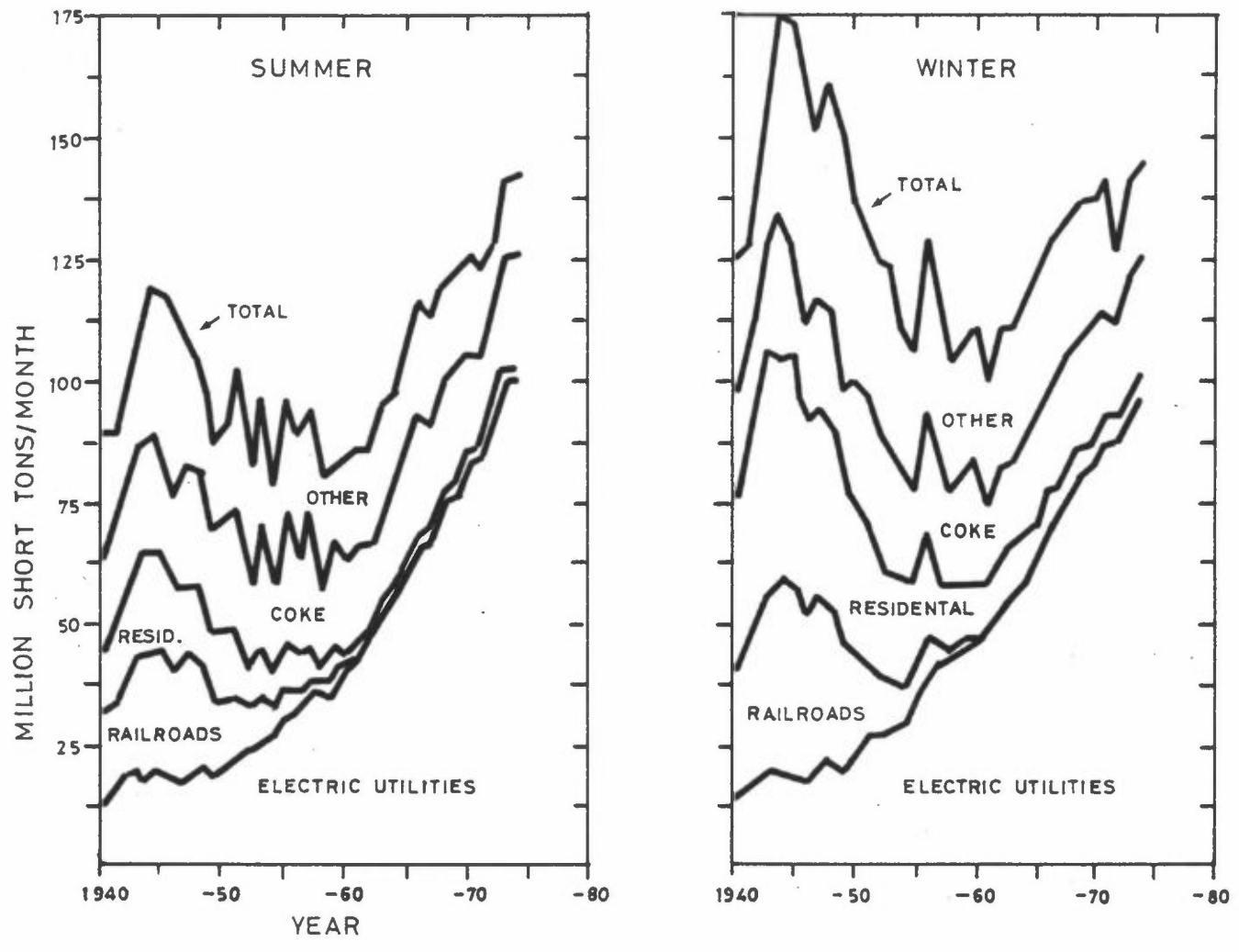


Figure 2: US winter and summer coal consumption 1940-1974. (After Husar et al. 1979).

acid, nitric acid, ozone and photochemical oxidants, are formed.

In the other group we find various trace elements, such as zinc, cadmium and lead, and some highly stable groups of organic compounds, such as the polycyclic aromatic hydrocarbons (PAH), known for their carcinogenic properties, and a number of chlorinated hydrocarbons, e.g. the polychlorinated biphenyls (PCBs) and a number of widely used pesticides (DDT, Lindane, etc.) known for their toxic and mutagenic effects (see, for instance, the proceedings of the international conference on "Chemistry - Man - Environment" (GDI, 1980)).

The accumulation of mercury, cadmium, DDT and PCBs in the natural food chains and the dramatic effects sometimes observed on predatory fish and birds, as well as humans, when exposed to excessive concentrations of these compounds, have led to an extensive hunt for other substances, which may have similar effects. Several other trace elements have been listed (Mn, Ni, As, Sb, Se) as potential suspects, and a number of organic compounds are investigated for their carcinogenic and mutagenic effects.

Water and carbon dioxide are released in larger quantities than any of the other substances. Only in extremely cold situations, does the water vapour from combustion represent a problem. However, the carbon dioxide concentration in the atmosphere has increased about 15% in the course of this century. If the annual world consumption of fossil fuels continues to increase at the present rate (~4%), this may cause a measurable change of the climate of the northern hemisphere by the beginning of the 21st century (Kellogg, 1977).

The combustion of fossil fuels, incineration of waste, and many industrial processes emit particles over a wide size range. The very small particles with an aerodynamic diameter below 0.1 μm agglomerate within hours to particles in the size range from 0.1 μm to 2-3 μm , often called the accumulation mode (Whitby, 1978). Because of reduced mobility, the growth of the particles in the upper part of this range mainly takes place by small particles

being attached to the larger ones. Through various chemical reactions many of the gaseous components may also end up as particles in this size range.

The main sources of particles larger than 2-3 μm are mechanical processes and weathering. While the small particles have a high content of sulphates, nitrates, soot and fly ash with adsorbed trace metals and organic components, these larger particles are characterized by soil elements as silicon, aluminium, iron, calcium and magnesium. The larger particles have an appreciable sedimentation velocity, and they are normally not transported over long distances, unless strong winds bring the materials high up into the troposphere. Occasionally soil material from the eastern USSR has been identified in Scandinavian fall out. Sahara dust, usually transported towards the West Indies by the trade wind, has deposited substantial amounts of soil on Cap Verde and the Canary Island (Rahn et al., 1979). An incident involving transport of Sahara dust led to the observation of "red rain" in S.E. England in 1968.

The particles in the accumulation mode are more closely associated with the long range transport of pollutants. The agglomeration of small particles and the formation and evaporation of cloud droplets result in particles with a mixed composition. The presence of fine particles of variable chemical composition therefore indicate that new materials have been added to the original aerosol.

Sooner or later most of the man-made pollutants are deposited on the earths surface, but mercury and many of the hydrocarbons, can be re-emitted by sublimation to the atmosphere after deposition and thereby redistributed. Such secondary emission is necessary to explain the amounts of mercury and chlorinated hydrocarbons found in many areas, and it may result in a general transfer of volatile pollutants from warmer to colder regions. Some pollutants, e.g., chloro-fluoro-methanes (freon), are not deposited on the earth surface at all, but remain in the atmosphere until they are broken down by ozone and photochemical reactions. For these and other highly volatile components the atmosphere itself serves as the main sink.

3 ATMOSPHERIC TRANSPORT

The air pollutants may be considered as injected into a system of atmospheric transport and circulation processes. The range of transport is limited by the residence time of the pollutants as controlled by the chemical persistency of the components and their rates of deposition. The ultimate dispersion is bounded by the dimensions and dynamic structure of the atmosphere.

Relative to the earth, the troposphere represents a very thin layer of air. If a distance of 1500 kilometers, say Paris to Oslo, is represented by 15 cm on a map, the mean height of the troposphere, 10 km, will be represented by 1 mm. In addition, the troposphere has a shifting and layered structure, and most of the transport of air pollutants takes place within the lower 1-2 km, often called the mixing layer. The exchange of materials with the stratosphere above the tropopause is a slow process, as demonstrated by the observed transfer of radioactive isotopes between the stratosphere and the troposphere following the nuclear bomb tests in the early sixties. This transfer was then found to have an effective half-life of 1-2 years depending on the height of the test. Only components which are chemically stable and not easily deposited, will be transferred from the troposphere to the stratosphere in significant amounts. A well known example is the chloro-fluoro-methanes or freons, and their reaction with the ozone layer.

Air pollutants are generally injected near the surface, or from chimney stacks of 100-200 m height. The initial concentration is rapidly reduced by small-scale turbulence generated by surface friction and thermal instability. After a while, the pollutants will be more or less evenly distributed within the mixing layer, and beyond a distance of 50-100 km, dependent on wind and stability conditions, dilution by small-scale turbulence becomes negligible. In the coarse grid systems used to describe the long range transport of air pollutants, the small scale turbulent dispersion can therefore be left out. On the other hand the need to include diurnal changes in wind and stability conditions complicates the situation. In the transition or mesoscale range of 10-100 km both

small and large scale effects have to be considered. This is therefore the least developed area of the air pollution transport modelling.

The mean residence time of the pollutants in the atmosphere may vary from a few hours for highly reactive components to several days and more for reactive substances, and it depends on the character of the underlying surface, atmospheric stability and precipitation frequency. To account properly for the regional and seasonal variations of these conditions represent a major problem in the modelling of the long range transport.

The stability of the atmosphere is affected by the diurnal variations in the radiation balance, the radiative properties of the surface, and the presence of clouds or haze. It is generally described by the vertical temperature gradient. A temperature decrease with height of 1°C per 100 m in dry air corresponds to the adiabatic temperature change which occurs when a parcel of air is displaced vertically. This is termed neutral stability. The actual value depends on the relative humidity of the air, and the thermal gradient is less pronounced in clouds.

In a stable atmospheric layer the temperature change is less than $-1^{\circ}\text{C}/100\text{ m}$, and vertical air movements will be suppressed. At ground level the temperature gradient may often be positive (inversion). If the temperature change is more than $-1^{\circ}\text{C}/100\text{ m}$, the atmosphere is unstable due to a temperature excess at the surface in relation to the air above. This results in vigorous vertical movements and air exchange. Such a situation occurs when there is a positive radiation balance during the day, and the unstable layer of air may typically extend up to 1-2 km during the day at mid-latitudes. On clear nights this is followed by the build-up of a nocturnal stable layer at ground level. This, in turn, is broken up during the next day. Measurements by air craft have shown that air pollutants are generally confined to within this mixing layer for transport distances up to 1000 km (Jost, 1973; Gotaas, 1980).

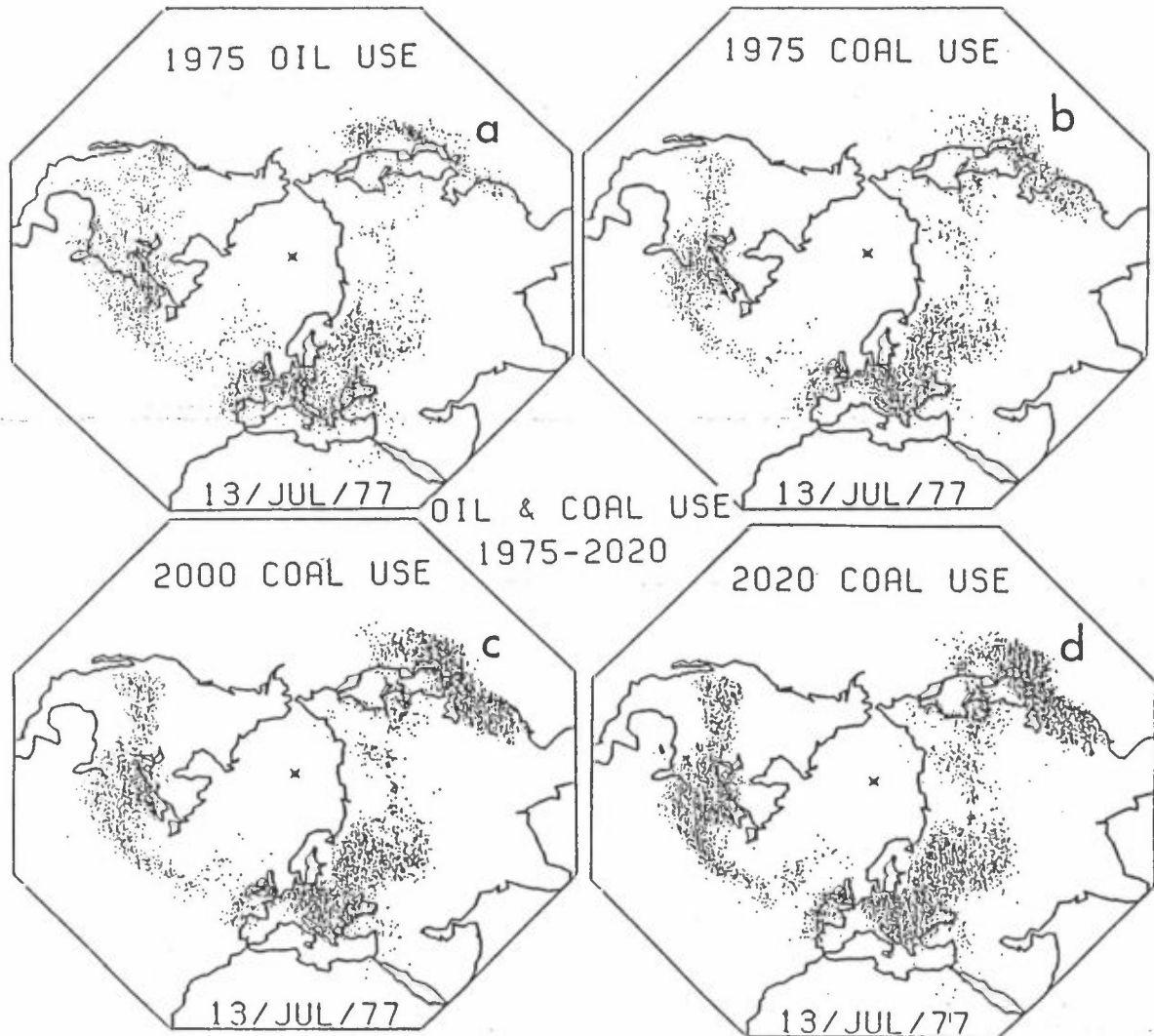


Figure 3: Dispersion in the westerlies of pollutants from the continents. (Husar and Patterson, 1979.)

(a) Oil use scenario for 1975 and (b,c,d) coal use scenarios for years 1975, 2000 and 2020 and their consequences on the spatial distribution of effluents assuming a residence time of 5 days. Most of the increase in coal use is expected in the U.S.A., U.S.S.R., and China.

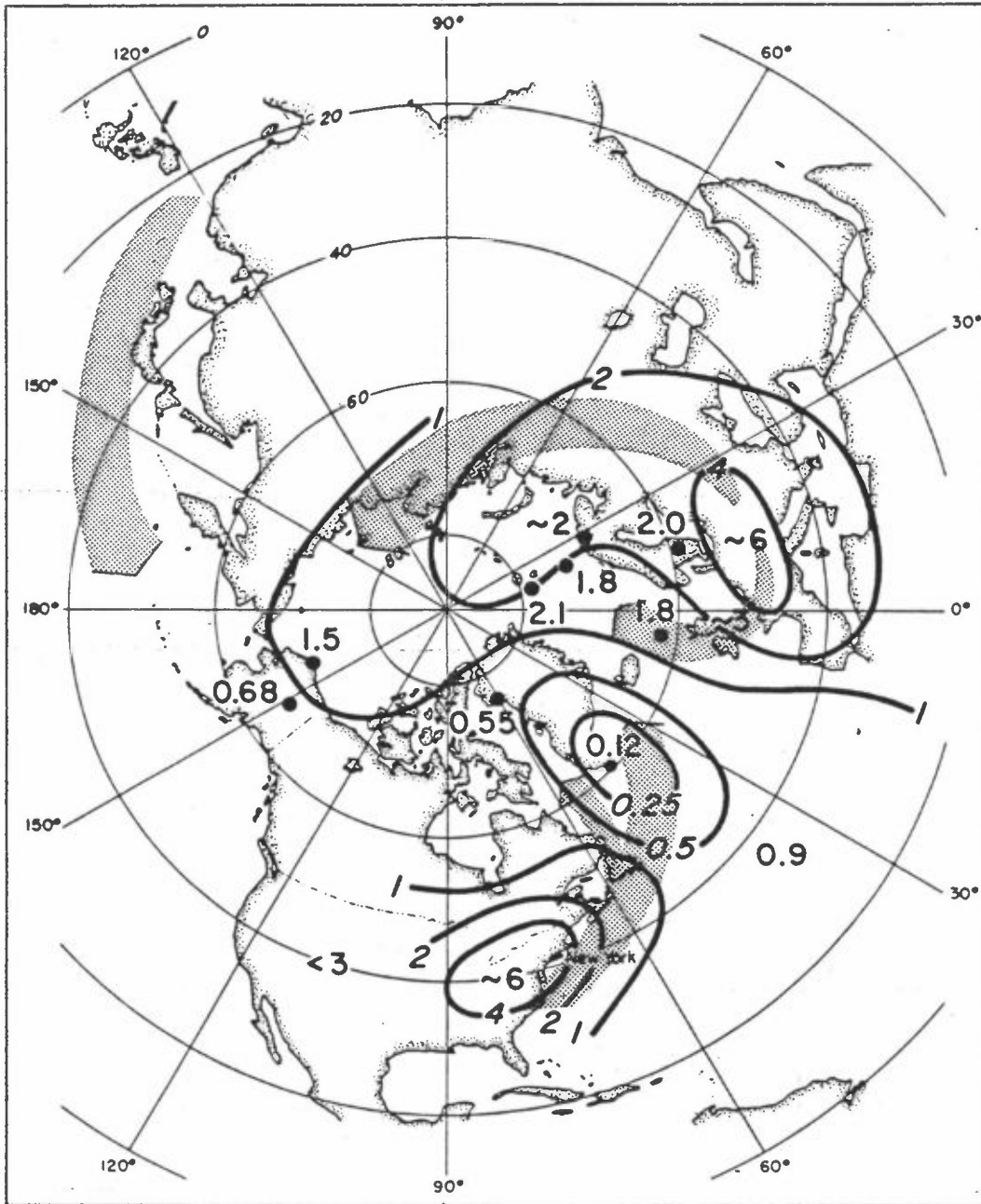


Fig. 4: Mean winter concentrations of nonmarine sulfate (μgm^{-3}) in surface aerosol of the Arctic and environs, after Rahn and McCaffrey (1979b). Possible pathways of pollutant aerosols from source regions to the Arctic. (Rahn and McCaffrey, 1979).

The effect of the diurnal changes in vertical dispersion has also been demonstrated in aircraft studies of power plant plumes by Husar et al. (1978).

The atmospheric mixing layer is also present over the sea, but here the diurnal variations are much less prominent, because of the more rapid heat transfer within the surface water. In certain areas, such as the North Sea, and the North Atlantic in winter, the sea is warmer than the air above, but in summer and at lower latitudes the situation is reversed. Temperature differences between the sea surface and the continents is the driving force of the diurnal land-sea breeze, which has dimensions of up to 100 km, and the large-scale monsoon wind systems which account for much of the systematic air transport in the tropical and subtropical regions.

Solar heating and radiation loss are also the driving forces of the planetary wind systems. Ascending warm air in the tropical region flows northwards and southwards, descending in the sub-tropical high pressure belts. This air will retain its momentum relative to the earth's rotational axis, so that at higher latitudes the air will move faster than the earth's rotation, resulting in a general west-to-east air movement known as the westerlies. Conversely, air moving from the sub-tropical high pressure belt towards equator will move from east to west in the equatorial trade winds. In a similar way subsidence of air over the poles leads to the polar easterly winds.

Thus, on the average and over longer periods of time polluted air from the east coast of north America moves out over the North Atlantic, pollutants released in Europe will move towards the east and the northeast, and pollutants from China and Japan will move out over the Pacific Ocean. An illustration of this general transport is given by the trajectory calculations of Husar and Patterson (1979) shown in Figure 3.

Over the cold polar areas there is a general subsidence of air brought in from lower latitudes, and a sharp boundary is formed between the cold air masses of the polar easterlies and the warmer air of the westerlies, known as the polar front. In the northern hemisphere this front is on the average situated further south in winter than in summer.

Along this boundary eddies are formed, which give rise to the wandering low pressures or cyclones at middle latitudes. In the northern hemisphere the air circulates counter clock wise around these low pressure areas which have an extension of characteristically 1000-2000 km. In the European region such low pressure regions and their associated precipitation fields incessibly move in from the northern Atlantic region across the continent in an easterly direction with an interval of a few days, and they have a dominating influence on the large scale air flow pattern.

On the basis of this picture, one would expect the main transfer of air pollutants to the polar regions to take place by subsidence of polluted air masses brought in at a high level. The isolated Antarctic continent seems to receive minute amounts of long-lived air pollutants in this way. The high Arctic, on the other hand, is surrounded partly by land and partly by sea areas. Recent experience has shown that in the winter this gives rise to a direct transport at low level of polluted air masses into the Arctic (Rahn and McCaffrey, 1979). Possible pathways are illustrated by Figure 4 and further discussed in Chapter 7.

The transport of the air pollutants is influenced by the conditions at the surface. Factors of particular importance are the radiation balance, which affects the mixing of the air in the boundary layer, and the surface friction. As the wind is reduced closer to the surface, its direction turns more and more into a flow from high to low pressure. In the northern hemisphere this results in a shift in wind direction to the left, and friction alone may account for a backing of 20-30° relative to the wind 1 km above the ground. In addition, topographical features may cause a channelling of the air. In a valley the resulting

wind may deviate as much as $90-100^{\circ}$ from the direction of the free wind before the air flow shifts into the opposite direction of the valley under neutral stability conditions.

In connection with the long range transport of air pollutants, the change of wind direction at ground level is of considerable significance, as it leads to a shear in the transported air mass. Vertical mixing of the air mass at a later stage may therefore result in a change of pollutant concentration. Over the oceans stability may prevent good mixing of air from different levels, and Pack et al. (1978) in a study of atmospheric transport across the Atlantic Ocean obtained better agreement with observed surface level concentrations by using a modified geostrophic wind, which was shifted 25° to the left and reduced to $1/3$ in strength.

At middle latitudes a nocturnal ground inversion is normally broken up by solar heating during the day. In winter at northern latitudes, when the days are short, and in the Arctic such inversions may persist for days and weeks, and winds of 8-10 m/s aloft have little effect in removing the heavy, cold and stable air masses. The snowcovered ground and the low sun angle in northern areas reduce the possibilities for the ground to absorb solar radiation, and evidently favour the development of ground inversions. Under such conditions, tall chimneys may be a very efficient means to improve the local air pollution situation.

In summer the sea is usually colder than the air, and a shallow layer of relatively stable air often develops next to the sea surface. This is of considerable importance for the long range transport, because such stable layers limit the dry deposition of gases and aerosols by reducing the turbulent mixing of the air next to the surface. The smoothness of the sea and snow covered areas adds to this effect. Thus, polluted air masses, which are brought with the winds from England or the European continent to Scandinavia, may lose little of their content of air pollutants in passing for 1000 km over the North Sea. The same is observed for polluted air masses passing across the great Lakes between Canada and the USA. In winter this also applies to polluted

air masses from eastern and western Europe passing over the snow-covered northern areas of Europe.

Most of the present experience with long range transport of air pollutants comes from measurements at middle latitudes in the northern hemisphere. In this region long range transport up to 1000-2000 km is frequently observed. The vertical extension of the polluted air masses is generally limited to 1000-1500 m, and individual trajectories are backed relative to the free wind. The residence time for aerosols and water soluble gases is generally of the order a few days. As the day to day value of the deposition rate is highly dependent on precipitation events, surface structure and atmospheric stability, the successful application of constant deposition rates merely indicates a relatively constant statistical distribution of these highly variable parameters. This simple picture is, however, not valid everywhere.

At lower latitudes, diurnal vertical mixing is much more violent. Also, wind systems tend to become more stationary in character, depending on the season.

Transport of atmospheric trace constituents to the Arctic is predominantly by subsidence of air brought in at higher levels.

Arctic and continental winter conditions are characterised by a negative radiation balance and a correspondingly shallow mixing layer. Vertical mixing is slow, particularly near the surface, and there is little precipitation and negligible dry deposition.

Studies confirm that the large scale and long term dispersion of the pollutants is governed by the general atmospheric circulation and the residence time. This has become particularly evident for the bulk transport within the mixing layer in the lower troposphere. In smaller amounts the pollutants are also dispersed to the higher troposphere. Aircraft measurements show that sulphates today constitute a major part and of the atmospheric aerosols also at higher levels (Georgii, 1978), and the content of chlorinated hydrocarbons in the Arctic snowpack can hardly be explained

otherwise. However, measurements in the upper part of troposphere are few, and the general transport of air pollutants into this region is largely unknown.

4 SULPHUR POLLUTANTS AND ACID RAIN FORMATION

In 1968 Odén showed that a central area in Europe with highly acid precipitation (pH 3-4) had expanded to include also the southern parts of Scandinavia. This observation was associated with the observed acidification of the water in rivers and lakes in Scandinavia, where in many places the fish population had disappeared. In addition, incidents of greyish snow were observed in areas remote from pollution sources. Chemical analyses showed a high content of sulphuric acid, soot, fly ash and other pollutants. These observations caused much alarm in Scandinavia, and in 1969 the matter was brought to the attention of the OECD. In the OECD project "Long range transport of air pollutants" (LRTAP) which was completed in 1977, the acid precipitation was quantitatively related to the emissions of sulphur dioxide in Europe (OECD, 1977; Ottar, 1978), the main source being the sulphur content of fossil fuels. The results showed that significant amounts of air pollutants were transported from the central source areas to regions more than 1000 km away.

These studies are continued in the "Co-operative program for monitoring and evaluation of the long range transmission of air pollution in Europe" (EMEP), which has been established under the auspices of the UN Economic Commission for Europe, with participation from both eastern and western European countries (ECE 1976). Some results from the OECD/LRTAP project which show the exchange of sulphur pollutants between European countries are given in Table 1. Data from EMEP confirm these findings (ECE 1980).

In North America long range transport of air pollutants is examined by several regional programmes. While the European and Canadian studies center on ecological problems resulting from the acidification of the precipitation, the USA emphasis was initially on air pollutant concentrations, health effects and

	BELGIUM	DENMARK	FRG	FINLAND	FRANCE	NETHERLANDS	NORWAY	SWEDEN	UNITED KINGDOM	CZECHOSLOVAKIA	GDR	POLAND	OTHER AREAS	UNDECIDED	SUM	EMISSION
Sweden 1974	7	30	30	10	10	6	6	100	40	8	50	20	30	100	500	415
1975	9	40	40	4	15	8	8	150	60	9	50	15	10	100	500	
1976	5	30	30	10	9	4	7	150	30	15	60	20	30	100	500	

(10³ tonnes S/year).

Table 1: Example of Exchange of sulphur pollutants between European Countries. (OECD, 1977).

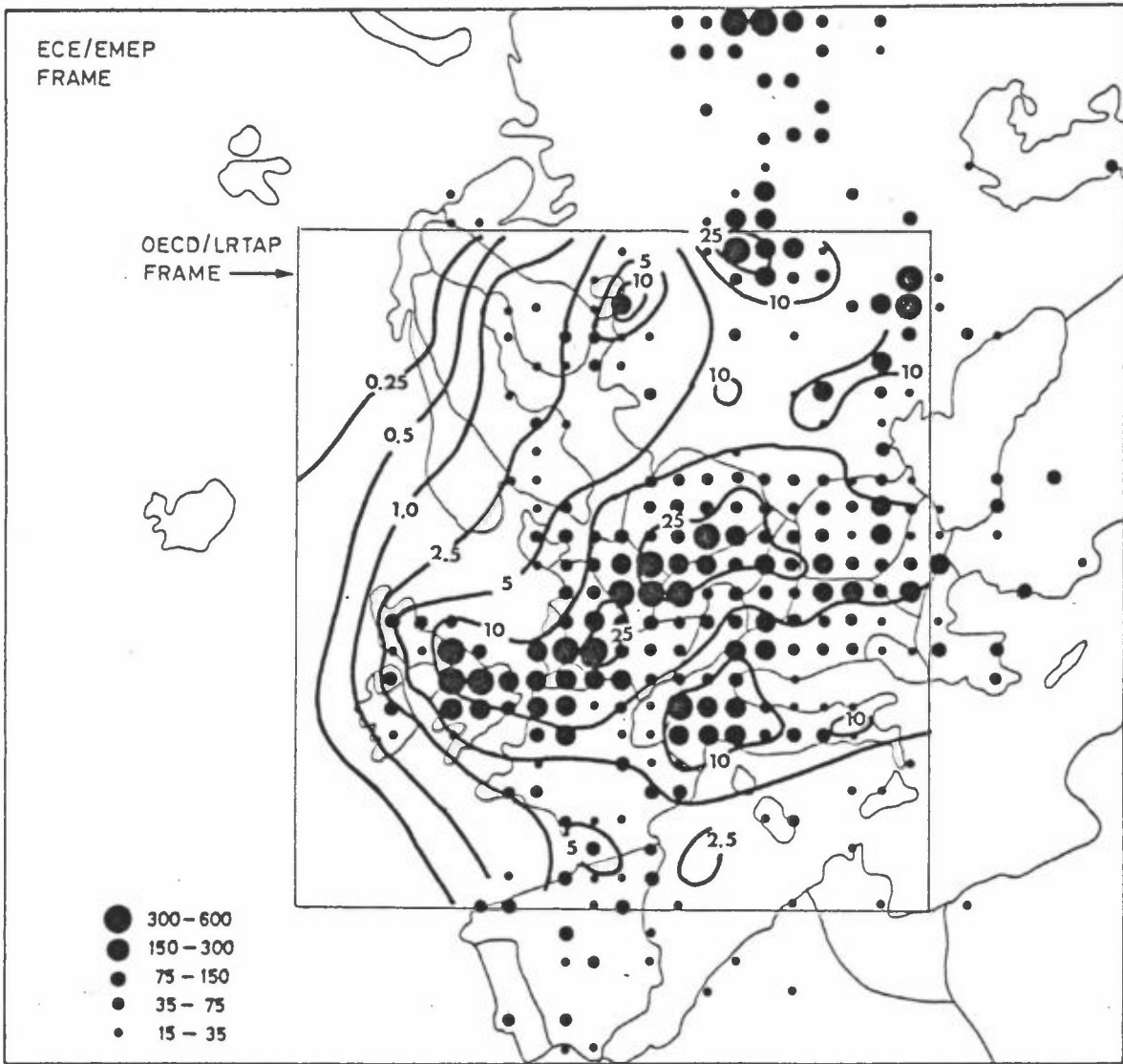


Fig. 5: Estimated sulphur dioxide emission in 150 km x 150 km grid squares for Europe 1978 (kilotonnes S/year) (Dovland and Saltbones, 1978), and annual mean concentrations of sulphur dioxide (1974) ($\mu\text{gSO}_2/\text{m}^3$), (OECD, 1977).

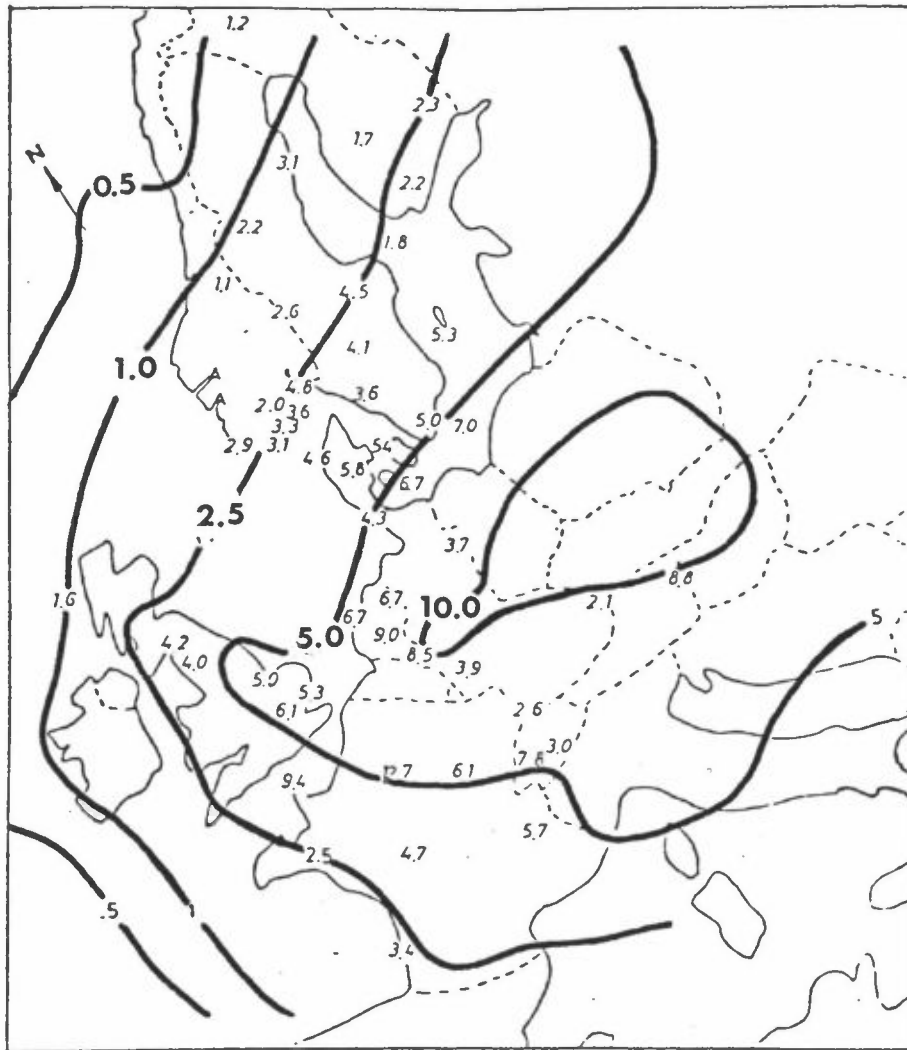


Figure 6 :

Estimated mean concentration field for particulate sulphate for 1974. Observed mean concentrations given by *Italic numbers*. Unit: $\mu\text{g SO}_4/\text{m}^3$. (OECD, 1977).

visibility. In later years this has changed, and is now an important issue between USA and Canada.

In the OECD/LRTAP project, wind trajectories and an emission survey for sulphur dioxide were used to calculate concentration fields of sulphur dioxide and sulphate aerosol using single layer atmospheric dispersion models (Eliassen, 1978). The dry deposition was assumed to be proportional to the air concentration, and the annual deposition of sulphate by precipitation was empirically found to be proportional to the product sum of observed daily precipitation values and sulphate aerosol concentrations. Constant chemical transformation and deposition rates were selected by fitting the model to daily measurements from more than 70 ground stations in the region. Aircraft sampling was used to obtain information on the vertical distribution of sulphur (Gotaas, 1978).

In the OECD/LRTAP study an emission survey for sulphur dioxide was established in co-operation with the participating countries. For other countries the survey was based on national fuel consumption data, collected from OECD and ECE, emission factors and population density. For some countries the accuracy is within $\pm 10-15\%$; in other cases the data are less accurate. The major emission areas are, however, sufficiently well defined for model calculations (Semb, 1979).

The maximum concentrations of sulphur dioxide are found near the major emissions, as shown in Figure 5 (OECD, 1977). In the central part of Europe the annual mean concentration of sulphur dioxide is about $20 \mu\text{g}/\text{m}^3$. The annual concentration pattern of sulphate particles is similar (see Figure 6), but because of the time required for sulphur dioxide to be transformed into sulphate particles the annual mean concentration level is lower (with maximum values of about $10 \mu\text{g}/\text{m}^3$), and the westerlies shift it further to the north-east.

The dry deposition of sulphur dioxide is a significant factor in the central part of the area and is responsible for the removal of about 50% of the total emission. Compared to this, the dry deposition of sulphate is of less significance. About 30% of the total

sulphur emission is removed by precipitation. Maximum deposition is found in orographic precipitation areas frequently exposed to polluted air masses, as seen in Figure 7 (OECD, 1977). Examples are the Scandinavian mountains and the Alps. The remaining 20% moves out of the area, and recent studies have shown that in winter considerable amounts of air pollutants find their way from Europe and the Soviet Union into the Arctic (Ottar, 1980a; Rahn et al., 1981).

The day to day situation is very different from this average picture. With southerly winds, concentrations of 20-30 $\mu\text{g}/\text{m}^3$ of sulphur dioxide and sulphate particles are frequently observed in the southern part of Scandinavia. For this area, more than 90% of the annually deposited sulphate comes from outside the region, and 50% of this may be due to 10 episodes with highly polluted precipitation. A similar situation is observed in other remote areas exposed to orographic precipitation. The main acidic component is sulphuric acid with an addition of 20-50% of nitrate and ammonium ions on an equivalent basis. The annual mean concentration of sulphate in precipitation in Europe from BAPMON data for the period 1972-76 (Wallén, 1980) is shown in Figure 8. Episodes with maximum acidity are often observed when highly acid particles are formed in air which has remained over the sea for several days (no ammonia emission), and later are scavenged by orographic precipitation. In 1978 an exceptional case of 10 mm precipitation with a pH of 2.5 was reported by the Meteorological Service in Iceland. Cases of pH 2.7 have been observed in Scotland and on the west coast of Norway.

The ecological effects of the acid precipitation in Norway have been extensively examined in the SNSF project (SNSF, 1980; Overrein et al., 1980).

The nitrates contribute significantly to the acidity of the precipitation in Scandinavia, but because of the general nitrogen deficiency of the vegetation in this area, ammonium and nitrate ions are quickly consumed by the vegetation. The acidification of the rivers and lakes is therefore mainly determined by the sulphate ions and accompanied by an increased concentration of aluminium hydroxyions. The acidity is particularly harmful to the fry and the aluminium is deposited in the gills of the fish. Similar effects are observed in areas in the eastern part of Canada and the USA.

Some discussion has been caused by the fact that the total amount of hydrogen ions in the soil cover is much larger than the annual amounts brought down by the precipitation. But the release of these hydrogen ions and the aluminium ions to the runoff is effectively limited by the amount of mobile anions. However, sodium is not exchanged to any significant extent by the humus, or coastal rivers would have been polluted by hydrochloric acid. As it is, sodium chloride from the sea salt largely passes through the system together with the sulphate ions.

Considering that the emissions of sulphur dioxide have increased only twofold since the middle of this century, while the concentration of air pollutants in remote areas may vary by a factor of 10-20, it may well be that incidents of acid precipitation have occurred for a long time without being noticed. Thus, fish kills in rivers in southern Norway, reported at the beginning of this century, may well have been the result of long range transport of sulphur pollutants. The decline in fish populations, which was examined in the 1920's (Dahl, 1927), but not related to the acid precipitation has, however, been much more dramatic in the last 30 years.

The mean acidity of the precipitation in North America for the periode 1976-1979 (RCG, 1980), is shown in Figure 9.

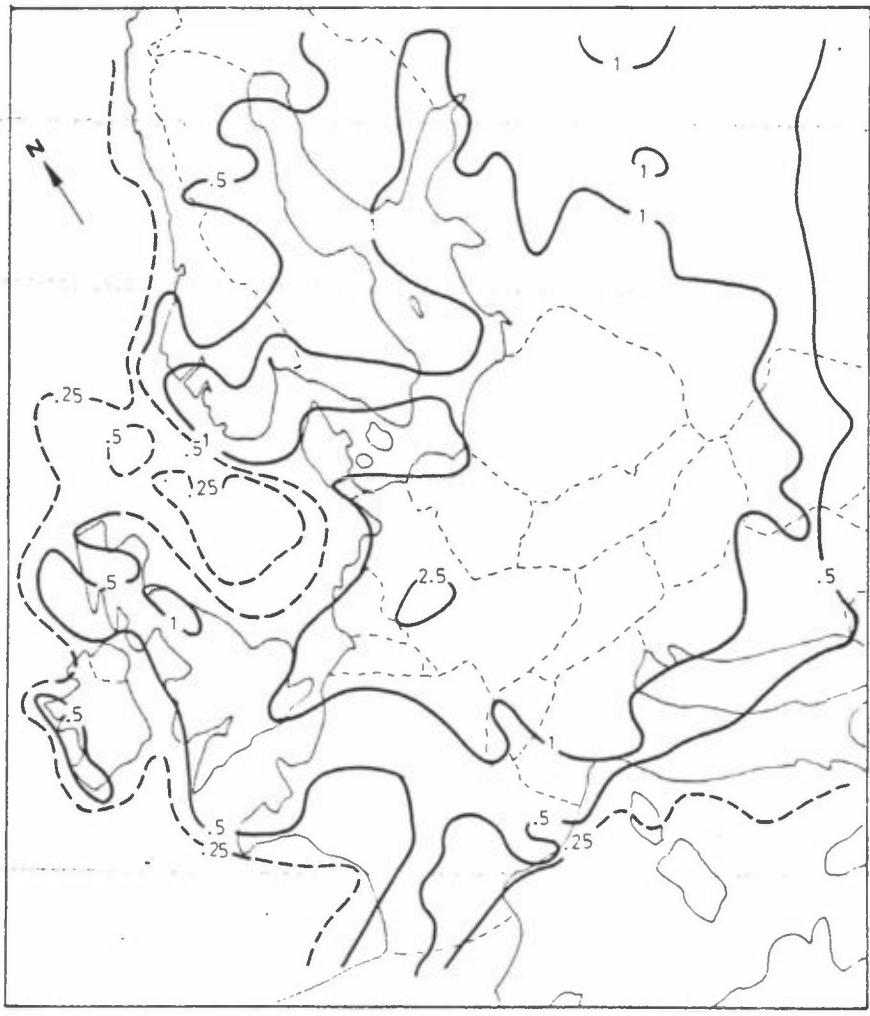


Fig. 7: Estimated sulphur wet deposition patterns for 1974. Unit: g S/m², (OECD, 1977).

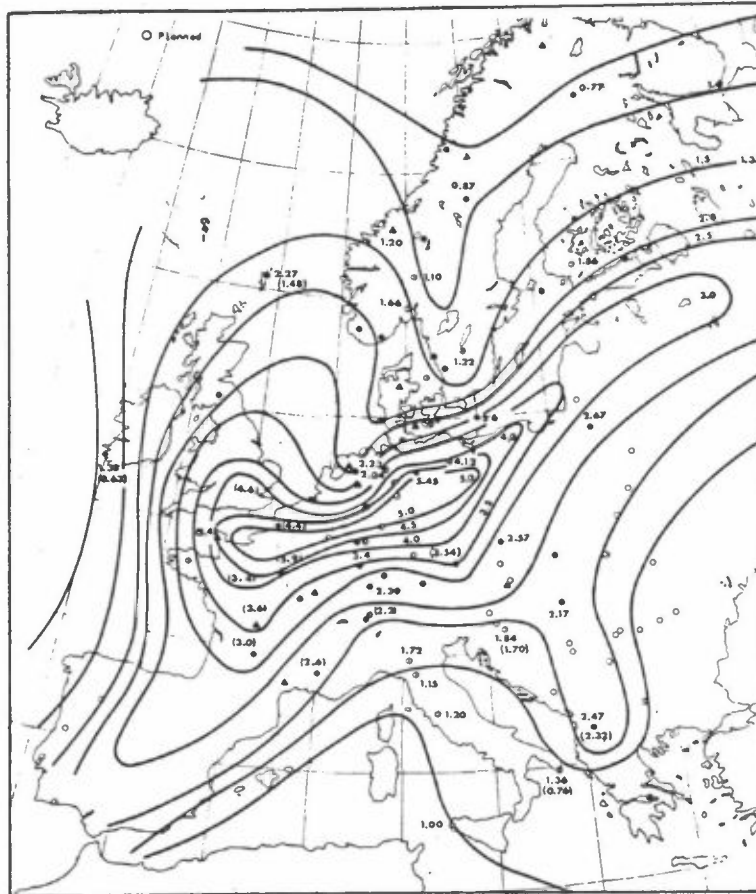


Fig. 8: Annual mean concentration of sulphate in precipitation ($\text{mgSO}_4 \text{l}^{-1}$) 1972-76 (BAPMoN data), (Wallén, 1980).

The maximum values (minimum pH) are located in the eastern part of the continent and closely related to the major emissions in the Ohio valley. In north-eastern USA and Canada, both deposition and sulphate concentrations are at a maximum in summer.

In Scandinavia the concentrations of sulphate in precipitation are generally highest during the spring, while the emissions of sulphur dioxide in Europe have a maximum in January (about 2 times the emissions in summer). This delay can be attributed to a precipitation minimum in Western Europe during the early spring, and more rapid conversion of sulphur dioxide to sulphate with increased solar radiation. The seasonal variation of the concentration of nitrate in precipitation is similar but with a longer maximum period (Joranger et al., 1980).

This reflects the different climates and fuel consumption patterns in Europe and North America. In Norway the precipitation at the present contains about equivalent amounts of nitrate and ammonium ions. In the 1950's this ratio was also very constant, but the concentration of nitrate ions was only 2/3 of the ammonium ions. The basic reason for this constant ratio seems to be that in north-western Europe the emissions of nitrogen oxides from industry and motorized traffic largely take place in the same regions as the agricultural activities. The higher ratio today indicates that the nitrogen oxide emissions have increased over the past years. It is interesting to note that in North America the emission of ammonia come from the mid-western agricultural areas, while most of the nitrogen oxide emissions come from areas further east. As a result the ratio between nitrate and ammonium ions in precipitation is much more variable.

The studies of the long range transport of the atmospheric sulphur pollutants, which were started in Europe in the 1970's, have shown that the air pollutants are more widely distributed than previously believed. The components which are transported over long distances as gases and as fine particles in the accumulation mode, include most of the pollutants and their secondary products.

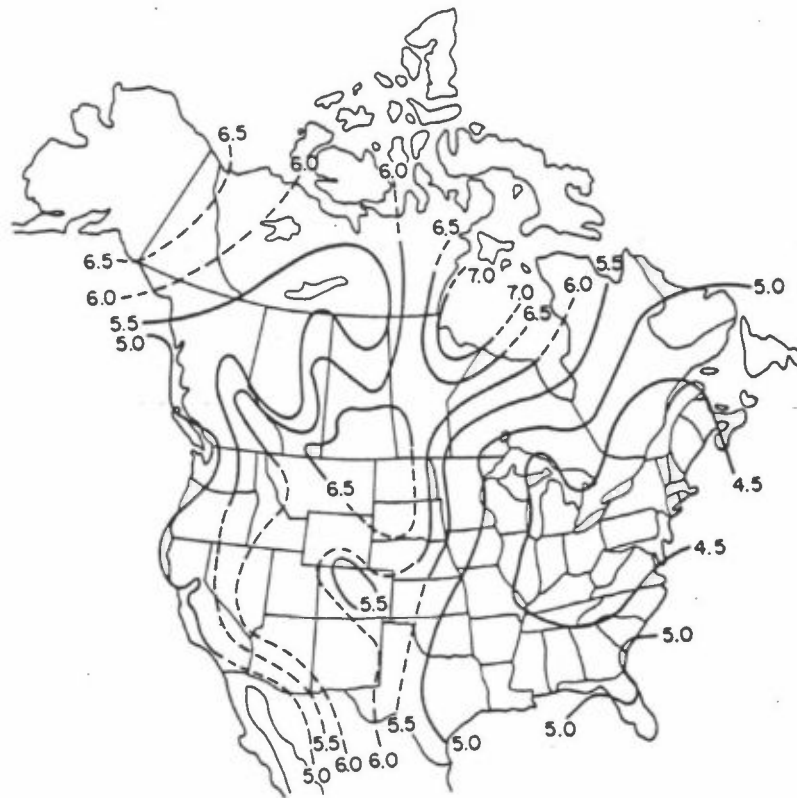


Fig. 9: Weighted mean pH of precipitation for North America for the period 1976-1979. Dashed lines indicate where data are sparse and thus only the general pattern is indicated, (RCG, 1980).

The acidity of the precipitation is mainly governed by its content of sulphate, nitrate and ammonium ions, and may to a large extent depend on the pathway of the polluted air masses. The ecological effects are not simply related to the acidity of the precipitation, but are the result of complex interactions in which all the major ions in the precipitation are of significance.

5 NITROGEN OXIDES AND OXIDANTS

The emissions of nitrogen oxides are mainly due to oxidation of nitrogen in the air during combustion processes. The main sources are motorized traffic, power stations, and space heating (Semb, 1979). In the large scale picture, process emissions are of less significance. High combustion temperature and an excess of air favours the formation of nitrogen oxides. Thus, modern diesel engines have about the highest nitrogen oxide emissions per unit of fuel. Some typical emission factors are given in Table 2.

In the atmosphere the nitrogen oxides give rise to a number of different chemical reactions. The nitric oxide (NO) initially formed in the combustion process is rapidly oxidized to nitrogen dioxide (NO₂). The emission is therefore usually given as the equivalent concentration of NO₂, and designated as NO_x. When exposed to sunlight in the atmosphere, NO₂ is decomposed to NO and atomic oxygen which reacts with molecular oxygen to form ozone (O₃). The NO is oxidized back to NO₂ by O₃ and the so-called photostationary equilibrium is reached. When organic components are added, however, a net production of O₃ is obtained. Initially, organic radicals and hydrogen atoms are formed by solar radiation. The hydrogen atoms combine with oxygen to peroxyradicals (HO₂.), which oxidize NO to NO₂ while hydroxyl radicals (HO') are formed (Atkins et al., 1972). In addition to an increased production of ozone, this highly reactive mixture of oxygen atoms and free radicals leads to the formation of various highly reactive organic peroxides and nitrates, as well as aldehydes and nitric acid. Photochemical reactions also play an important part in the homogeneous gas phase oxidation of sulphur dioxide. (For a review,

	Emission-factor kg NO ₂ /tonne fuel	Fuel consumption Tg	NO _x -emission Tg NO ₂
Hard coal			
Power plants	9	133	1.2
Industry	6	22	0.1
Other	2	24	0.05
Brown coal			
Power plants	4	137	0.5
Residual fuel oil			
Power plants	12	69	0.8
Refineries	8	19	0.15
Industry	8	95	0.75
Other	6	27	0.16
Gas/diesel oil			
Industry	8	24	0.2
Other	4	121	0.5
Transport	36	46	1.7
Motor gas			
Transport	25	90	2.2
Natural gas			
Power plants	1	336	0.3
Industry	0.3	642	0.2
Other	0.2	554	<u>0.1</u>
			9.0

Table 2: Fuel consumption and estimated NO_x emission within OECD Europe in 1975 (Semb 1979).

see Isaksen, 1979).

The composition of the reaction products depends on the initial concentration of the reactants and the reaction conditions. The concentration of photochemical oxidants are often reported in terms of the content of ozone, which is the main constituent and relatively easy to measure. However, ozone is also produced naturally in the stratosphere from where it is periodically brought down to the lower part of the troposphere. In order to avoid confusion, it is therefore desirable to measure other components of the photochemical oxidant mixture, such as peroxyacyl nitrate (PAN).

In polluted areas the oxidant production reaches a maximum in the afternoon, and the highest values are often observed some distance away from the main precursor emissions. During night there is no production of oxidants, and in the polluted air of a city the oxidants will rapidly be consumed in various oxidation reactions. The final products are nitric acid, various organic nitrates, aldehydes and organic acids. Oxidants which are moved out of the polluted area, may survive the night and give the photochemical reactions the following day an early start. In this way oxidants produced in one area may enhance the problems in areas more than 500 km downwind. Several such situations have long been known from USA (NAS, 1977; OECD, 1978).

In Europe oxidants were first noted in the Netherlands in the late 1960's (Guicherit and van Dop, 1977). By then, many believed that photochemical smog would only be found at lower latitudes with intense sun radiation. Later experience has shown that if the emissions of nitrogen oxides and organic components are large enough, photochemical oxidants can be produced up to 70°N in the summer season. (Schjoldager, 1977). A simultaneous increase of the ozone concentration has on several occasions been observed all over Western Europe. In southeastern Norway these elevated concentrations of ozone partly seem to be due to an influx of oxidants from UK and the Continent, which may enhance the oxidant production from local emissions (Schjoldager *et al.*, 1981).

However, more measurements of other oxidants (e.g., PAN) are needed in order to quantify the significance of national and external sources. This applies even more when the question about oxidant transport over still larger distances is raised.

The effects of the oxidants are well known from the photochemical smog experience in Los Angeles and many other cities in USA, and from Australia and Japan (OECD, 1978). These effects include eye irritation, unpleasant odours, reduced visibility, and vegetation damage. It may, however, be worthwhile noting that in Europe unpleasant odour is a more pronounced characteristics of the photochemical oxidants than eye irritation. This may not be surprising, when considering the complex composition of the oxidants and possible differences in the input of hydrocarbons, but it probably delayed the recognition of photochemical oxidants as a significant problem in Europe by many years.

The effects of long range transport of the photochemical oxidants primarily concern vegetation damage. The generally increased reactivity of the air also increases the oxidation rate of sulphur dioxide to sulphuric acid and the nitrogen oxides to nitric acid. According to Canadian forrest authorities an exposure for 2 hours to concentrations of 85 ppb ozone results in a reduced growth of coniferous forrests, but no visible damage. In the recent large scale attack by bark beetles on forrests in Oregon, trees which had been weakened by exposure to photochemical oxidants, were only important for the first generation of beetles (Dahlsten and Rowney, 1980).

In Europe during the last few years there have been large scale attacks by bark beetles on forest in the Mediterranean area and in Scandinavia. To what extent photochemical oxidants may be a contributing factor is difficult to say. In these cases there are always a number of causes playing together, e.g., an exceptionally dry summer or extensive wind fall, and after the first year the attack has built up enough strength to continue on its own.

6 THE CHLORINATED HYDROCARBONS

In the chlorinated hydrocarbons some or all of the hydrogen atoms are substituted by chlorine. This results in molecules which are almost insoluble in water, and the vapour pressure is increased. The chlorinated hydrocarbons are inflammable, chemically very stable and they do not occur naturally.

The world production of DDT and other polychlorinated pesticides today amounts to more than 500 000 tons/year. The world production of polychlorinated biphenyls (PCB) has been much reduced during the 1970's and PCB is now mainly used in closed systems as hydraulic liquids and as insulation in electrical transformers. In the USA PCBs are no longer produced. At present the world production is estimated to about 10 000 tons/year. However, several hundred thousand tonnes of previously produced PCBs are probably still in use. (NAS, 1979). Another substance in this group is hexachlorobenzene, with a world production of about 5 000 tons/year. All these substances have a vapour pressure in the solid state, and they are found today in samples of air, soil and biological materials all over the world (Edwards, 1973).

For most of these substances the acute animal toxicity is low, because the organism is only able to take up minute amounts from contaminated food. But because of their lipoid solubility, the polychlorinated hydrocarbons accumulate in the fat tissue. They affect the nervous system, and the placenta is unable to protect the embryo against the mutagenic effects of these poisons (Peerebom-Stegeman and Peerebom, 1980).

The toxic potential of these chemicals is further illustrated by 2,3,7,8 - tetrachlorodibenzo-p-dioxin, which, as contaminant of a commercial product, was responsible for the mutagenic effects of the spraying of forests in Oregon and the incident in Seveso in Northern Italy. The cancerogenic effect of the polychlorinated hydrocarbons are discussed by Epstein (1980).

Observed concentrations of the more abundant polychlorinated hydrocarbons in the atmosphere vary from a few ng/m³ in remote areas to several hundred ng/m³ in areas where these substances have been used. In precipitation the concentration varies from a few ng/l to several µg/l. A comparison of the concentrations of chlorinated hydrocarbons in precipitation and air indicates that only a few percent is deposited by precipitation. This probably corresponds to the aerosol fraction, which is known to be efficiently scavenged by precipitation (Atkins and Eggleton, 1971).

The relatively low concentrations of chlorinated hydrocarbons in precipitation as compared to the air, imply that the atmosphere serves not only as a means of transportation, but also as a substantial reservoir. Wheatly (1973) estimated that as much as 15% of the total DDT, produced up to that time, might be contained in the atmosphere. In the case of hexachlorobenzene, an even larger part of the total amounts emitted may be contained in the atmosphere.

Until recently, there have been considerable difficulties in sampling and measuring the concentrations of chlorinated hydrocarbons in the atmosphere. Most of the evidence on long range transport is therefore based on analyses of materials in which the accumulation of these compounds cannot be explained by local emissions. Thus, concentrations of 10-50 ppb of chlorinated hydrocarbons are found in the fat of penguins in the Antarctic. Residues of 40 ng/l in the antarctic snow indicate that more than 2000 tonnes of DDT may have accumulated there.

In undisturbed soils chlorinated hydrocarbons are found in the upper 20 cm, usually with a maximum concentration 5-10 cm below the surface. In tropical and subtropical areas, where DDT has been extensively used, the concentration of DDT in the soil is very low, indicating an almost complete re-emission to the atmosphere (Spencer 1975). Chemical analysis of Swedish soils in 1968 (Sömme, 1971) showed DDT concentrations of 0.05-0.2 ppm in the upper 15 cm. The total amount in Swedish soils was estimated to 2500 tonnes. The deposition by air pollution fallout was esti-

mated to 600 tons/year, while only 60-70 tons were used in Sweden in 1968. Since then the use of DDT has been abandoned in Sweden.

An estimate of the PCB content of the Baltic Sea has recently been made by Kilstrøm and Berglund (1979). Assuming a concentration of 0.1 ng/l in the water, the total content becomes approximately 2 tonnes. The annual catch of fish removes 0.3-0.6 tonnes of PCBs per year, while the fallout of air pollution for the Baltic area is estimated to 6 tonnes PCBs per year. This may explain why the concentrations of PCBs in biological samples from the Baltic Sea have not decreased since the use of PCBs was restricted in the late 1960's. The same applies to the Great Lakes in N.America. The production of PCBs in the USA was stopped in 1979, but still the concentrations in the lake waters are increasing, and more than 50% of the input comes from the atmosphere (Eisenreich et al., 1981).

In the atmosphere over Norway concentrations of hexachlorobenzene up to 0.1-0.2 ng/m³ are found. The annual emission to the atmosphere in Norway is estimated to about 30 kg, which is far too little to explain this. The concentration of PCBs in precipitation at 22 stations in Norway varied from 2-7 ng/l (Lunde et al., 1976), with most of the PCBs adsorbed on particles. Neither can this be explained by Norwegian emissions.

Because of their chemical stability, the chlorinated hydrocarbons may be emitted to the atmosphere from contaminated soil or water bodies over a long period of time. Thus, the surface may be a source or a sink, depending on temperature, air concentrations, surface saturation, etc. This will redistribute the material over the earth's surface, and when a balance is reached, one would expect the amounts evaporated in a year to be approximately equal to the amounts deposited. This implies that the reduced rate of evaporation in colder areas must be compensated for by a higher surface concentration in order to balance the annual mean air concentration. Over a longer period of time one must therefore expect an increased surface concentration of polychlorinated hydrocarbons in the colder regions due to atmospheric transport from warmer areas (Ottar, 1980b,c). Ocean currents and exchange between

the atmosphere and the sea surface may also be an important part of the process. Because of the re-emission of these substances to the atmosphere, the long term dispersion patterns may be very different from the short term dispersion patterns, which so far have been studied in connection with local and regional pollution problems.

The polychlorinated hydrocarbons are slowly broken down when exposed to solar radiation in the atmosphere, and also to some extent in metabolic processes. However, when buried in the soil and protected against sunlight, their lifetime is estimated to be many years. When re-emission and redistribution of these substances are taken into account, it may well be that present estimates of the residence time are far too low.

Since the beginning of the 1970's, the use of DDT and PCBs has been restricted in many countries. Data from Switzerland and Scandinavia show that the DDT level is reduced subsequent to these measures. In Switzerland the PCB levels are also reduced, but in Scandinavia this does not seem to be the case (Brevik and Bjerk, 1977); Schüpbach, 1980).

The transfer of polychlorinated hydrocarbons from warmer to colder regions will slow down as the temperature is reduced, and one would expect a geographical separation of the components according to their volatility. Further, the local level will be determined by two factors: the input from local usage and the transfer from outside regions. If the substance has been used locally in relatively large amounts, restrictions should slowly lead to a reduction of the contamination level, as the substance is either broken down or re-emitted to the atmosphere. If the transmission from other countries dominates, national restrictions would have little effect.

Observations in Europe indicate that in the case of DDT the burden due to earlier local releases gradually disappears, while contributions from outside, because of the low volatility of DDT, are too small to compensate for the loss. Gradually the concentration

will then approach a level corresponding to a balance between the import and removal of DDT from the outside. In the case of the PCBs the volatility is higher, and the amounts used locally in Scandinavia are very small. Accordingly, the contamination levels may still increase in areas where local emissions have been very low.

Recent analyses of air samples from Bear Island and Spitsbergen show that the chlorinated hydrocarbons have also found their way into the Arctic. The samples were collected in September 1980, a period with little or no transport of pollutants into this region (see next chapter). The results showed 1-2 pg/m³ of DDD and DDE, traces of DDT, and 40-70 pg/m³ of HCB. Less chlorinated benzenes were present in amounts up to 6-30 pg/m³, which α -hexachlorocyclohexane showed concentrations in the range 500-1300 pg/m³. This result is consistent with transfer of these substances to colder regions by deposition and re-emission over a long period of time.

7 AIR POLLUTION IN THE ARCTIC

The Arctic haze was first reported by Mitchell (1956). Flying north of Barrow in Alaska, he observed a layer of fine particles 1-2 km above the polar ice. For a long time the cause of this haze was a riddle to the scientists. A closer examination of the phenomenon was not undertaken until the 1970's. The first analyses of samples collected from aircraft indicated that soil dust from Central Asia could be a source, but more extensive measurements at Point Barrow and at Ny-Ålesund on Spitsbergen showed that the aerosol contained considerable amounts of typical pollution components such as lead, vanadium, and even soot from the combustion of fossil fuels (Rahn and McCaffrey, 1980).

At this time the OECD/LRTAP project had shown that sulphur dioxide and sulphate from the industrialized areas in Europe could be traced to remote areas 1-2 thousand km away. Already in 1972 measurements in Northern Norway showed a number of cases with

high aerosol concentrations due to transport of polluted air masses from central Europe. And it has since been shown that sulphate is a dominating component also in the arctic aerosol (Larssen and Hanssen, 1979).

Through an informal co-operation between institutions in several countries a network of measurement stations has now been established in the Arctic, see Figure 10 (Rahn, 1980a). At the stations high volume samples of aerosols are collected and analysed for water soluble components and for 20-30 trace elements, mainly by neutron activation. At the Norwegian stations, daily measurements of sulphur dioxide and sulphate in precipitation are also performed, in accordance with EMEP routines.

A survey of the present knowledge on air pollution in the Arctic (Arctic Conf., 1980) shows that a periodic transfer of polluted air masses to the Arctic takes place in the winter season. This may increase the concentrations of pollution components 40-50 times (see Figure 11). The main component is sulphate, but the aerosol also contains a number of trace elements, e.g., vanadium and manganese, from industrial sources outside the Arctic. Furthermore, the content of Pb-210 shows that the air masses are of continental origin. At present, elementary carbon (soot) in the particles is analysed in order to improve the basis for evaluating the effect of the particles on the global radiation balance (Rosen and Novakov, 1981).

The main industrial areas in the northern hemisphere are all situated in the zone of the westerlies. The dispersion of air pollutants in this wind belt was first discussed by Kellogg et al. (1975). A distribution, calculated by Husar and Patterson (1979), is shown in Figure 3. These calculations do not, however, explain the high concentrations observed in the Arctic during winter. Possible pathways are indicated in Figure 4, and probably the most important source areas are Europe and parts of the Soviet Union (Rahn, 1980b). This air flow is explained by the moving low pressure areas in the Norwegian Sea and the formation of a high pressure

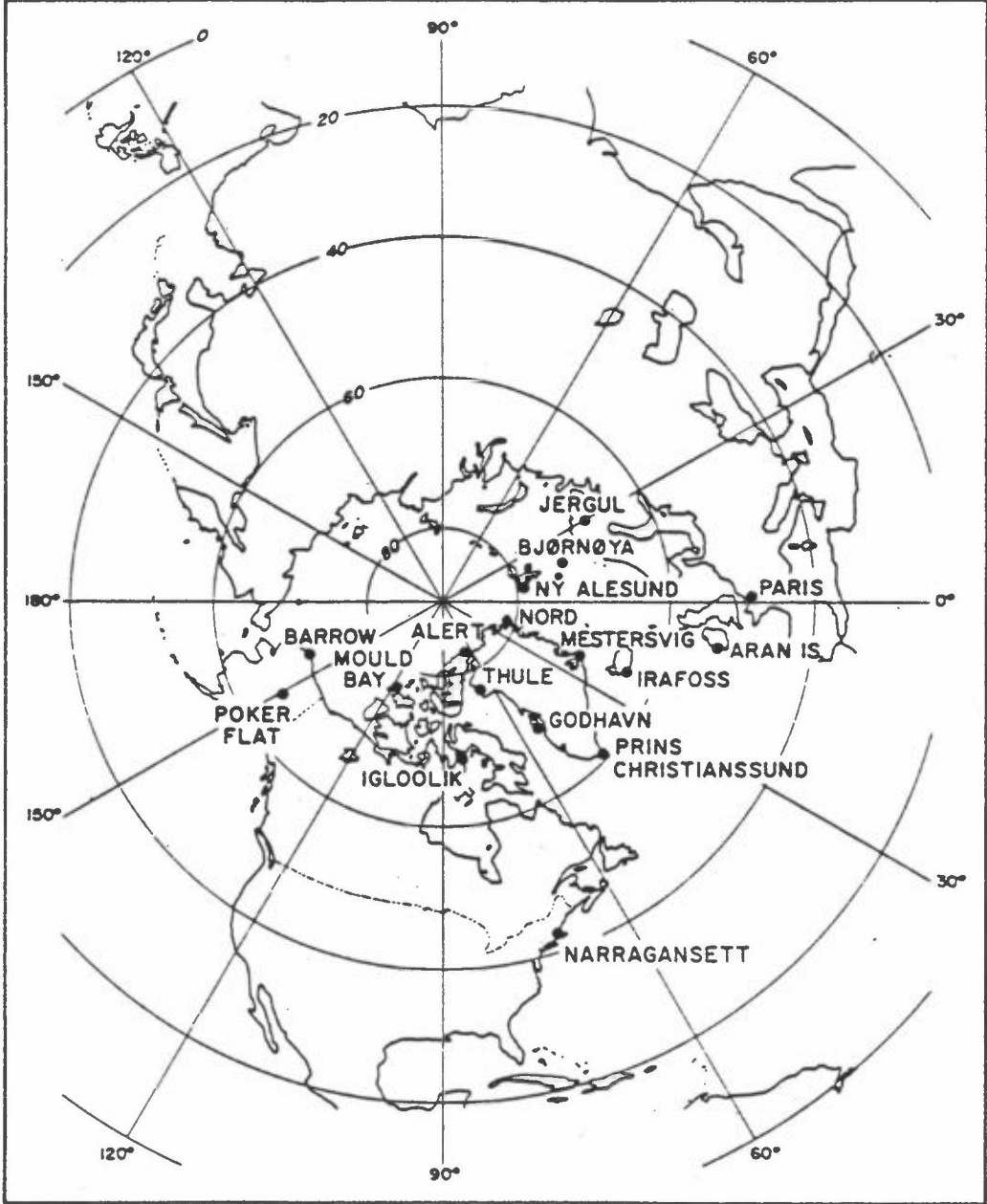


Fig. 10: Sites of the Arctic Air-Sampling Network in 1980, (Rahn, 1980a).

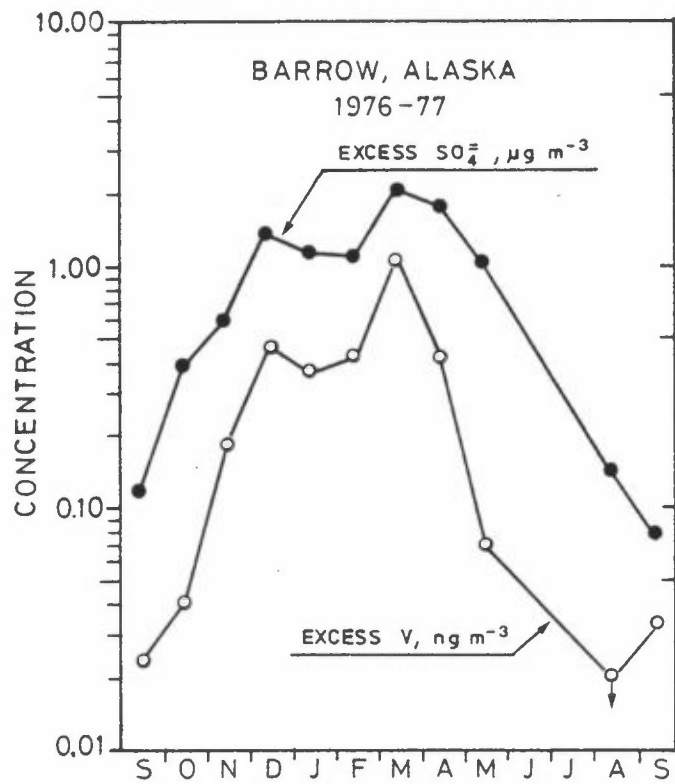


Fig. 11: Monthly mean concentrations of excess sulphate and excess vanadium in Barrow aerosol 1976-77, (Rahn and McCaffrey, 1980).

centres over the cold Asian continent in winter. The result is a periodic transfer of polluted air masses across the northern part of USSR into the arctic region. Measurements indicate that these pollutants are dispersed over the whole polar region and are the main cause for the haze observed at Barrow. A significant point in this connection is that the highest concentrations of sulphate and sulphur dioxide at the Bear Island station occur with northerly winds. The same applies for the aerosol concentrations at Barrow.

In summer there is no similar transport. Partly the meteorological situation is different, and partly the deposition of pollutants on the ground and vegetation is much larger in the summer time. The air pollutants from the east coast of North America do not seem to reach the Arctic in significant amounts along the route indicated in Figure 4. This may be due to deposition by precipitation. Neither do pollutants from the industrial areas in China and Japan seem to reach the Arctic.

Within the industrialized regions of North America and Europe the residence time of gases and aerosols in the atmosphere is estimated to a few days. The winter observations in the Arctic require a residence time of 10-20 days. Several factors contribute to this. In winter the wet deposition is very low in this region, and the dry deposition is also at a minimum. The generally dry air and the lack of ammonia emissions and sunshine, result in a low transformation rate, which explains the relatively high concentrations of sulphur dioxide observed at Bear Island and Spitsbergen.

The transport of air pollutants to the Arctic involves distances up to 10 000 km. Detailed analyses of the chemical components along the route, could give opportunities for evaluating the changes in composition which the substances undergo in the atmosphere. The soot content is of particular interest. As a conservative tracer it may serve as a yardstick for other components and it has recently been shown that the sulphate to carbon ratio may be a useful indicator of the age of the aerosols (Rahn et al 1980).

8 GLOBAL DISPERSION OF AIR POLLUTION

With constant emissions, the mean concentrations of air pollutants over an area will reach a level determined by the balance between emissions and deposition. The annual mean concentration field for sulphur dioxide in Europe (Figure 5) is an example of this balance. If the deposition rate is reduced, the concentration field will expand in directions given by the general atmospheric circulation, and observations show that in winter the sulphur concentration fields are extended into the Arctic.

For components with very long residence times in the atmosphere, dispersion through the atmosphere will build up an increasing background concentration. However, as the atmosphere represents a thin sheet of air compared to the dimensions of the earth, enhanced mean concentrations will always be found over the major source regions.

The carbon dioxide concentration of the atmosphere is the result of a balance between consumption by vegetation and absorption in the oceans, and emissions from the biological decay of organic materials and from the combustion of fossil fuels. Since 1860 the emissions have increased exponentially by about 4% p.a. At present, the amount of carbon dioxide released annually by the combustion of fossil fuels is about $6 \cdot 10^9$ tonnes. As a result the mean concentration levels in the atmosphere have increased about 15% during this century, from about 295 to 340 ppm. If the emissions remained constant at the present level, the CO_2 concentration over some 40 years would be reduced to an equilibrium level considerably lower than the concentration observed today. If, on the other hand, the world consumption of fossil fuels continues to increase at the present rate, the concentration of CO_2 may reach 600 ppm in another 40 years.

The main sink for carbon dioxide is the oceans below a depth of 100-200 m. Because of the slow exchange between the atmosphere and these water masses, the exponential increase of the emissions has led to an air concentration considerably higher than the equilibrium value for constant emissions at the present level (Kellogg, 1977; IIASA, 1978).

As carbon dioxide absorbs infrared radiation from the earth's surface, heating of the atmosphere results, the so called greenhouse effect, and it is estimated that this effect alone could increase the mean temperature of the earth by about 1°C early in the next century. Because of the circulation in the atmosphere and the oceans, there will probably be no temperature change at the Equator, while the temperature in the polar regions may increase by $3-5^{\circ}\text{C}$.

Because of the long residence time of carbon dioxide in the atmosphere, the short term variations of the carbon dioxide concentration are small in relation to the mean value of 340 ppm, see Figure 12. Tracking of the carbon dioxide plume from a city would therefore require very accurate measurements, and at present there are only a few stations in the world where the carbon dioxide concentration has been measured with great precissions over a longer period of time (Barrow, Hawaii, South Pole, American Samoa). If emission data and atmospheric dispersion models could be used to calculate the large scale CO_2 concentration pattern, the data basis might be improved significantly.

In order to avoid effects from the natural CO_2 -cycle, the Arctic would seem to be a suitable starting place for such studies. For the winter season, Rahn has recently found (Rahn, 1981) that short term variations of a few ppm in the content of carbon dioxide of the air at Barrow are accompanied by a parallell variation in the content of non-crustal vanadium in the aerosol, (see Figure 12). The higher values are connected with northerly winds, which indicates that the observed fluctuations of the carbon dioxide concentration in the winter months are related

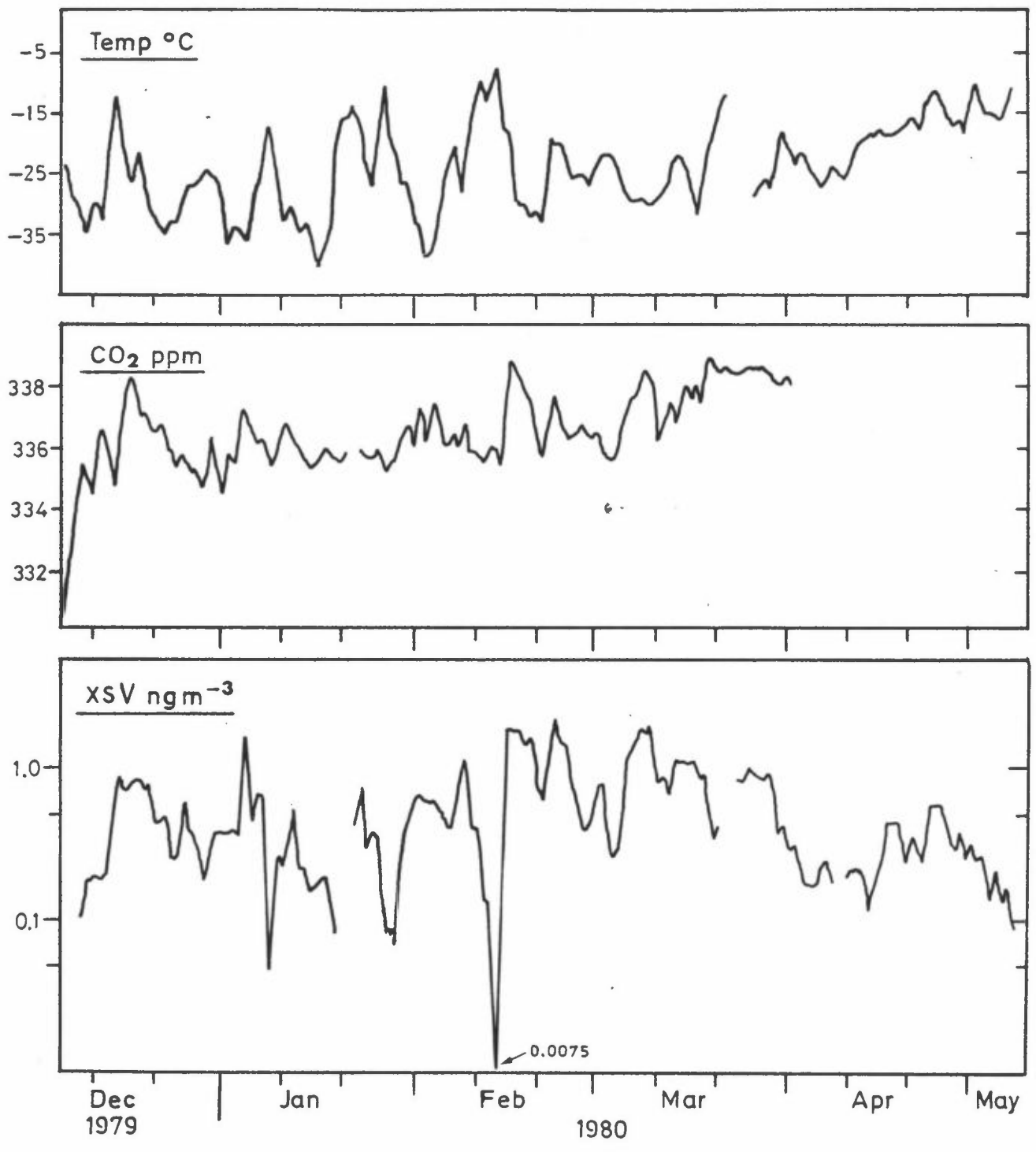


Fig. 12: Winter concentrations of CO₂ and non-crustal V at Barrow 1979/80 and temperature, (Rahn, 1981).

to the influx of polluted air masses from Eurasia. By April the vanadium concentration drops to very low values, as this influx comes to an end. At the same time the CO₂ concentration becomes less variable, as would be expected if subsidence of air from higher levels now becomes the main transference process for air to the Arctic. Considering the distance of several thousand kilometers from Eurasia to the Arctic, this means that concentrations, significantly different from the global annual mean, are maintained over the source regions, and that studies of the atmospheric dispersion of carbon dioxide in the Arctic might contribute significantly to our understanding of the CO₂-problem.

In addition to the "greenhouse effect" of carbon dioxide, changes in amount and composition of the atmospheric aerosol will also disturb the radiation balance in the atmosphere (Kellogg *et al.*, 1975). Aerosols reflect part of the incoming radiation, and thus tend to reduce the temperature at the earth's surface. An increased concentration of carbon particles will absorb radiation, and raise the temperature of the atmosphere. In addition the pollutants may affect the cloud cover. The net result of these and other effects is difficult to estimate, in particular these effects will have to be separated from still unexplained natural climatic variations (Bolin, 1975). It seems probable, however, that early changes may be more easily observed in the Arctic than elsewhere.

In connection with possible global effects of the air pollutants, the increasing use of chemicals, which do not occur naturally, must also be mentioned. A well known example is the chlorofluorocarbons or freons. The main use of these substances is in spray-cans and refrigerators. Plumes of freons are therefore observed downwind of larger cities. The freons are not deposited at all, and the only factor which limits the accumulation of these substances in the atmosphere is their breakdown by solar radiation and chemical reactions. This takes place mainly in the ozone layer of the stratosphere, and calculations show that it will take years before equilibrium is established between emissions and breakdown of the freons. Estimates indicate that the amounts released up to now may lead to a 10% reduction of the ozone layer,

and a corresponding increase in ultra-violet radiation at the earth's surface. An important question is if this is the only way in which freon is removed from the atmosphere.

It has been known for many years that the heavier polychlorinated hydrocarbons and many other organic compounds participate in the long range transport. More recently the polycyclic aromatic hydrocarbons have been added to the list (Thrane and Michalsen, 1981) are re-emitted to the atmosphere by sublimation after initial deposition. Much of the deposition passes via adsorption to the aerosols and deposition by precipitation, and observations indicate that a systematic transport of these substances takes place from the warmer to the colder regions. This takes considerable time, and in the process the more volatile components are separated from the heavier ones. It has been suggested that a substantial part of these substances accumulate in the atmosphere and may affect the radiation balance. In particular, many of the organic components are much more efficient absorbers of infrared radiation than carbon dioxide, (Kondratjev and Bunakova, 1978), which may compensate for their lower concentrations.

The ecological effects of the global pollution of the atmosphere are partly related to the possibility of climatological changes, and partly to the transfer and accumulation of pollutants within the natural food chains. For many of the substances very little is known about the amounts which are transported and deposited, their chemical degradation, and their accumulation in the living organisms.

The task to clarify these problems is clearly enormous. With the measurement techniques and the modelling capacity generally available in most countries today, problems of this magnitude will not be solved. However, the techniques are steadily improving, e.g., air craft sampling, remote sensing, and satellites have hardly been used yet in connection with the long range transport of air pollution. The problems also require a closer international cooperation between nations, and in this connection it should be remembered that with the enormous production capacity of the

chemical industry of the world, and the delayed reaction of the climatological and ecological systems to this atmospheric input, we may only have about 20 years to solve the problems, if they are not to run out of control.

9 MODELLING OF THE LONG RANGE TRANSPORT

The general purpose of transport modelling will often be to identify sources in order to assess the impact of future developments. When large distances are involved, one has to dispense with many details in the model, and the problem often is to find a practical compromise between desired information, available data and computer capacity.

Aircraft measurements show that most of the air pollution transport in Europe takes place below a mixing height of 1-2 km (Gotaas, 1978). Observation also show, that 100-200 km downwind of a source area, turbulent mixing causes no further dilution of the pollutants. Beyond this distance, depending on the weather conditions, the pollutants will be evenly distributed in the airmass and only slowly removed by dry deposition. The only process which can rapidly clean this air, is precipitation scavenging.

The long range transport of these polluted air masses is conveniently described by wind trajectories in a grid system. The geographical resolution of the trajectories is limited by the available synoptic wind data. Sometimes topography or stability data may be used to obtain further details of the wind fields, but the geographical scale of the transport also sets a limit to the space and time resolution, which can be given a meaningful interpretation.

Under neutral stability conditions, turbulence and meso-scale meandering will cause the plumes from neighbouring sources to merge at a downwind distance 10-20 times their separation. Under stable conditions, the individual plumes may be identified over

much longer distances, but the stability normally varies during the day. Thus, there is little point in using a grid system much finer than 100-150 km to examine the transport over distances of 1000 km or more, because finer details in the concentration field will be due to contributions from nearby sources and not to the long range transport. The same reasoning applies to the measurements used to verify the model calculations. They should as far as possible be representative of the grid element and the time resolution used in the model. In the oxidant case this is a major problem, because the relatively fast chemical reactions, which lead to the formation of oxidants, require a small and unnecessarily detailed scale for a description of the long range transport.

Regional emission surveys, which can be used with atmospheric dispersion models to estimate the observed concentrations, have only been worked out for a few of the major air pollutants. For most of the minor components such inventories are not available. In this connection the question has been raised, if measurements and trajectory analysis can be used to identify source areas. To some extent this is possible, as shown by Prahm et al. (1979). If the substances can be assumed to originate from the same source areas the major components, simple proportionality may also be used as a first estimate (Söderlund, 1981).

The geographical distribution of sulphur dioxide emissions in Europe is shown in Figure 5, and based on data collected in the OECD/LRTAP and EMEP-projects and estimates from population density (Dovland and Saltbones, 1979; Amble, 1981). For larger areas the emissions are approximately proportional to the population density, with an addition for areas with a particularly high degree of industrialization. The emissions of nitrogen oxides largely follow the same pattern (Semb and Amble, 1981). In this case about 1/3 of the emissions originate from traffic, but because the traffic density depends on the other activities, an approximate proportionality is obtained for larger areas. The geographical distribution of the sulphur dioxide emissions in North America in Figure 13 (NRCC, 1981) shows that most of the emissions take place

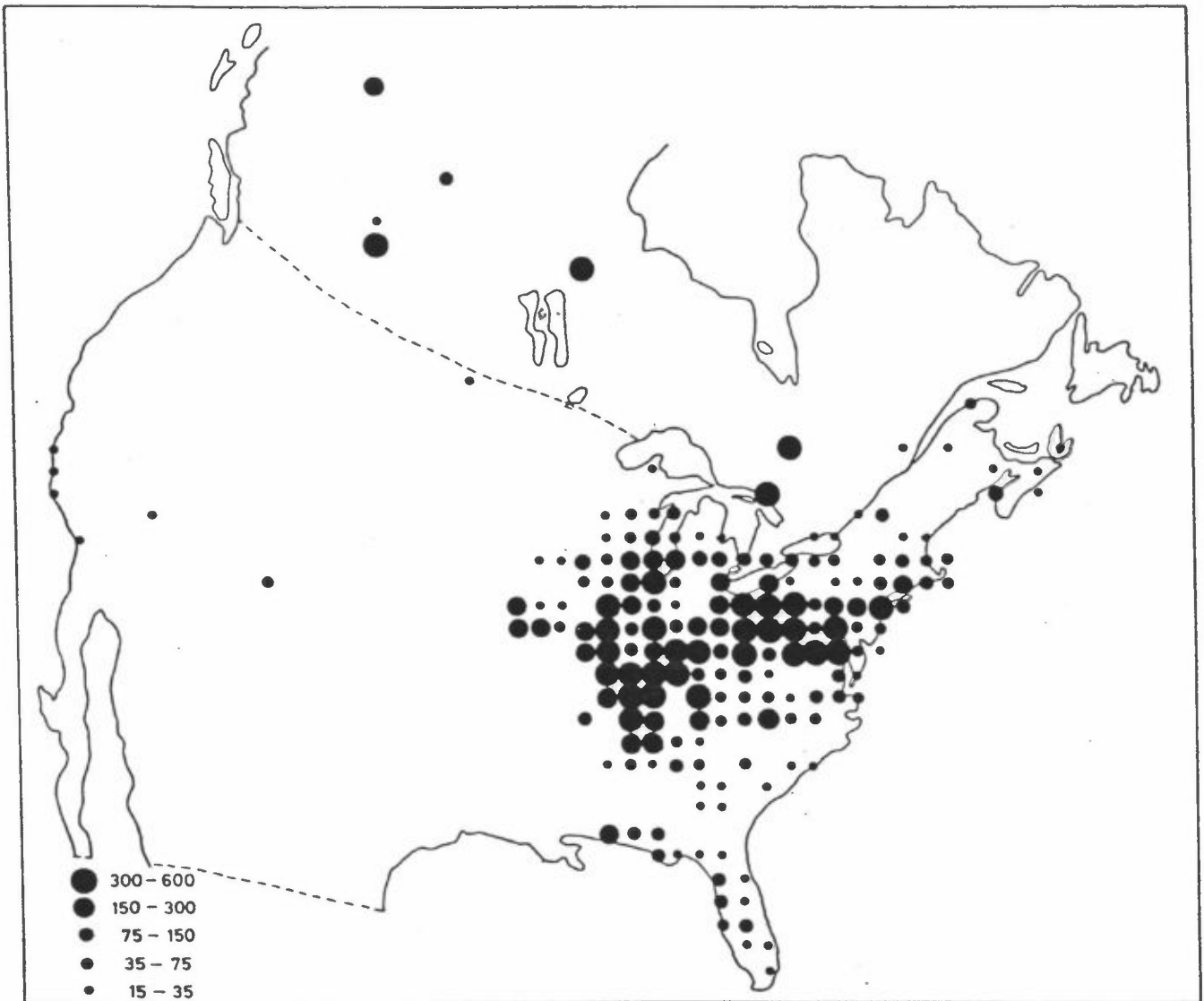


Fig. 13: Sulphur dioxide emissions in North America, 1970-75, (NRCC, 1981).
Unit: Kilotonnes SO_2 /year.

in the eastern part of the North American continent. Emission surveys for nitrogen oxides and hydrocarbons show similar distributions (NRCC, 1981).

For the large areas involved in the long range transport of air pollutants, precise information concerning all emissions is seldom available. It may therefore be useful to take a closer look at the information contained in an emission survey. The location of the major sources of emission is the most important. This information is usually correct and limited only by the space resolution of the grid system. Thus, if the back trajectory from the observation point passes a grid element with large emissions, elevated concentrations will be observed, if the meteorological data are reliable (sector analysis). Second in importance is the relative magnitude of the emissions. Usually a distinction is made between large point sources (power stations, larger industries) and area sources (space heating, traffic, and small industries). The emissions in the first group are often well known, while an accurate assessment of the area sources is very laborious. Estimates are therefore usually made from population density, fuel consumption data, and emission factors. Finally, the general background emissions from sparsely populated areas may contribute significantly to the total because of the large areas involved but have no effect on the distribution pattern.

In connection with the long range transport of air pollutants, diurnal variations in the emission rates are usually negligible. Seasonal and weekend variations will, however, be reflected in the measurements. This is usually handled by superposing a time variation on the estimated daily mean emissions.

In the OECD/LRTAP project two types of trajectory models were used to calculate the advection of the polluted air masses (Eliassen, 1978). In both models air parcels, representative of each grid element, are moved along air trajectories, and additional air pollutants are picked up when passing other grid elements. Simultaneously, pollutants are removed by dry and wet deposition or by chemical reactions. The forward trajectory model was used

to calculate the concentration field each 12 hours in order to follow the development. With the forecast weather data, this model was also used to predict episodes of air pollution for the planning of measurements.

In the back trajectory model of the OECD/LRTAP project, the concentration in each grid element was calculated from 48 hour back trajectories. In the present EMEP program 96 hour back trajectories are used in order to reduce the amount of pollution of unknown origin. In this model the contributions to one grid element from all other elements are easily separated, and the model is regularly used to calculate the exchange of sulphur pollutants between the European countries. In both these models, complete mixing of the air within each grid element is assumed, and lateral dispersion is neglected. The calculations are checked by comparison with measured daily mean values.

In a different numerical approach by Husar and Patterson (1979), each source is simulated by a stream of equal air pollution quanta. As a quantum moves along the trajectory, a random displacement simulates the meso-scale dispersion of the plume. A main advantage of this model is that the lateral (and, if necessary, the vertical) dispersion is introduced as an explicit parameter, independent of the grid size. For models on a global scale, this may be an essential feature in order to avoid errors from the assumed complete mixing within the grid elements. However, if the chemical reactions which the pollutants undergo in the atmosphere, are of the second order with respect to ambient concentrations, e.g. photochemical oxidant formation, considerable complications arise.

In these Lagrangian models the changes of concentration are described in the air as it moves along the trajectory. In the Eulerian models, the concentrations of air pollutants are calculated simultaneously for all grid element by balancing the emissions and deposition with the air flow through each grid element. In its simplest version the components of the wind vector are used to distribute the pollutants to neighbouring grid elements. This introduces an artificial lateral dispersion, called pseudo-

diffusion, which may be acceptable in a city model because it more or less corresponds to the turbulent dispersion within the area. In long range modelling with large grid elements rather elaborate advection methods have to be used in order to avoid systematic errors (Egan and Mahoney, 1972, Christensen and Prahm, 1976). A survey of these models has been given by Eliassen (1980).

Statistical approaches are also used. Generally, the physical model represents a relationship between emissions, meteorological data and observed concentrations or deposition. If observations are available for a long period of time, statistical functions can be calculated from the observed concentrations and used to predict the concentration field from weather forecasts. Also statistical analysis of the differences between observed and calculated values may be used to improve parameter values in the model. This is in area in which very little has been done so far. Methods have also been developed to calculate annual mean concentrations from average wind fields or the statistical distribution of trajectories (Bolin and Persson, 1975, Fisher, 1978).

Most of the long range dispersion models are single-layer models, often with a constant mixing height. In such models the effect of nocturnal ground inversions cannot be handled. Therefore 24 hourly measurements will fit the model better than 6 hourly measurements. In order to include such diurnal variations one has to use a two-level model, or a perturbation of the vertical concentration profile within the grid element. The main problem in this connection is often to provide measurements to verify the results of more detailed calculations.

How far pollutants will move depends on the wind speed along the trajectory and the residence time of the specific pollutants in the atmosphere. The residence time primarily depends on the chemical stability of the component under relevant atmospheric conditions and the rates of dry and wet deposition (Garland, 1978). For some substances also the possibility of re-emission of previously deposited pollutants has to be considered. The chemical stability

depends on the presence of other reactants, air temperature, humidity, and radiation conditions. The dry deposition rate depends on the ground cover (water, vegetation, snow) and the vertical mixing of the air. Precipitation scavenging is very efficient for aerosols, but for gases it depends on the solubility of the component. For less soluble gaseous components initial adsorption by the aerosols may therefore be the more important pathway of deposition.

The residence time of the gases and particles to some extent also depends on whether the emissions take place near the ground or from tall stacks, which may discharge the pollutants above an inversion layer and thus prevent contact with the ground until the pollutants have moved far away from the sources. The significance of this difference for the mean transport of air pollutants over a period of time, however, should not be over-rated. When assessing the annual mean emissions of sulphur dioxide from European cities in the OECD/LRTAP project, this difference was estimated to 5% (OECD 1977). On a day-to-day basis, the difference may, however, be much larger.

Sedimentation by gravity is negligible for the fine particles and the dry deposition takes place by impaction, preferably on thin structures and sharp edges, and by interception and diffusion. The dry deposition of gases is determined by their rate of absorption, which depends on solubility and biological factors, such as daily variations of the photosynthetic activity level in a canopy. Thus, the type of surface is important.

In practice, the deposition rate of gases and particles is often characterized by a deposition velocity estimated from the time it takes to reduce the concentration in a vertical column when complete mixing is assumed. It must be emphasized that this deposition velocity is a relative measure, valid only under similar weather conditions. For grasslands the deposition velocity of sulphur dioxide is about 1 cm/sec, while the value for particles is only a few mm/sec. For snow-covered land the dry deposition rate of particles is only a few tenth of this value (Whelpdale and Shaw,

1974; Dovland and Eliassen, 1976), while for forested areas the deposition velocity for sulphate particles may be considerably larger (Fowler, 1980, Wesely and Hicks, 1979, Dollard and Vitols, 1980). Physically, dry deposition may be assumed to consist of two parts; the turbulent diffusion which brings the pollutants in contact with the surface and the adsorption or absorption of the substances by the available materials (Garland, 1979). If absorption is very efficient, as for instance for sulphur dioxide in water or vegetation, the deposition velocity may be controlled by the turbulent mixing of the air and can be calculated from measurements of the vertical concentration profile. If the absorption is slow, the air concentration may be approximately constant with height. Because of this behaviour, dry deposition rates cannot be measured in a simple way, and there is a general lack of reliable data.

The scavenging by precipitation is a complicated process, which is not too well known. It can be separated in two main steps: the nucleation of cloud droplets and their uptake of fine particles and soluble gases, and the washout by the falling precipitation below cloud level (Scott, 1978; Hales *et al.*, 1981). In the precipitation process ice nuclei are formed at the top of the clouds. In falling through the cloud, these ice nuclei pick up cloud droplets and form rain drops, snowflakes, etc. Dependent on the circumstances, these falling hydrometeors may pick up gaseous components in the air below the cloud. The absorption of highly soluble gases, as SO_2 , NH_3 and HNO_3 , seems to be of importance in both steps.

In order to obtain an idea about the actual situation from ground level sampling of air and precipitation, one may use the observation that in a normal rain storm at middle latitudes, about 1 ml of H_2O is precipitated from each m^3 of air in the cloud. With a 100% scavenging by precipitation, 1 ng/m^3 of a substance should give $1 \text{ } \mu\text{g/l}$ in the precipitation. Some typical analyses for the long range transport of air pollutants to Scandinavia across the North Sea are shown in Figure 14 (OECD 1977). In this case the high concentrations of nitrate and sulphate ions in

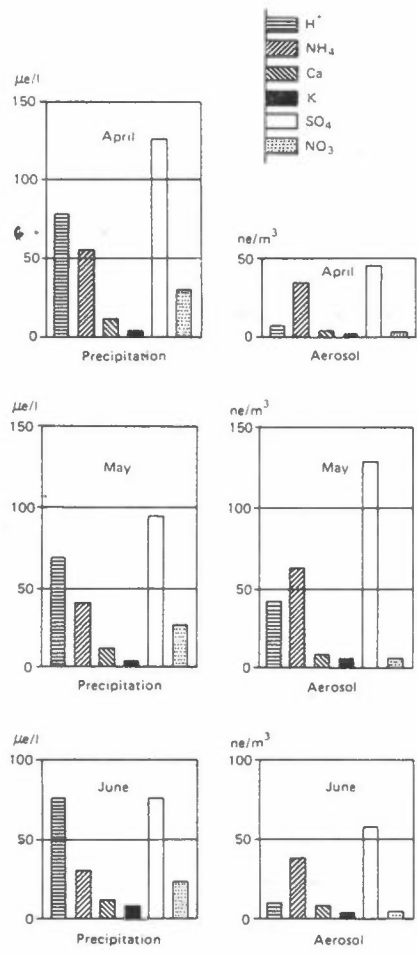


Figure 14: Concentrations of water soluble compounds in precipitation and aerosols at Birkenes, April-June 1975. (OECD, 1977).

the precipitation, relative to the aerosols, indicate that absorption of sulphur dioxide and gaseous nitric acid has taken place.

The residence time of the pollutants in the atmosphere is limited by their deposition. Available information on the dry deposition rates of gases and aerosols is generally limited to results of special laboratory and field investigations (Garland, 1979). Although there is considerable evidence of variations in the dry deposition velocities for different surfaces, seasons, and weather conditions, constant deposition rates are generally used. This is not a satisfactory approach, particularly when transport over very long distances is considered. As a first improvement, one might introduce different deposition rates for summer and winter, and for land and sea areas. However, in order to learn more about the dispersion process, independent information concerning these deposition rates is required. A simple validation of the model is unsatisfactory in this respect.

Wet deposition may be estimated, if precipitation data are available as functions of space and time. As the local precipitation is highly variable, mean annual precipitation data are often used to estimate approximate values for the wet deposition.

From a modelling point of view, one may distinguish between two types of chemical reactions in the atmosphere. In the simple case constant transformation rates can be used. A good example is the formation of sulphate particles from the oxidation of sulphur dioxide to sulphate. In this case the emissions from each grid element may be handled independently, but the situation becomes complicated if the reaction rates depend on the concentrations of other components present in the atmosphere. The result then depends on the background level and contributions from upwind sources, in addition to other variables, such as radiation, temperature and relative humidity. A well known example is the formation of photochemical oxidants, and an important question is whether available experience can be used to develop simplified procedures of calculation.

The chemical composition of the particles is influenced by other substances present in the air. An equilibrium is rapidly established between ionic components in the particles or droplets and the corresponding gaseous components, i.e., $\text{NH}_4^+/\text{NH}_3$, $\text{NO}_3^-/\text{HNO}_3$, Cl^-/HCl , $\text{SO}_4^{2-}/\text{SO}_2$. Particles formed over the sea are often particularly acid, because of the low partial pressure of ammonia. If later these particles pass over agricultural areas, they are rapidly neutralized by ammonia, at least at ground level. On the other hand, ammonium sulphate particles which pass over the acid forested soils in Scandinavia, have been shown to give off ammonia (Brosset, 1979).

In the particles, chloride and nitrate ions may be expelled in the form of gaseous hydrochloric and nitric acid by acid sulphates. Thus, the chloride from the sea salt component may be driven off as hydrochloric acid, which may be absorbed by larger particles the clouds, and the washout by the falling precipitation (Hales city aerosol are black because of their soot content. This soot has a graphite structure and is an efficient adsorber for gaseous organic components.

It may be mentioned that chemical reactions also can take place in samples of particles collected on filters, particularly if large and small particles are not separated. The pressure drop across the filter may also cause evaporation of the more volatile components. The chemical analysis may then give a distorted picture of the true airborne composition of the aerosol.

The observations mentioned above, show that the residence time of a chemical species in the atmosphere basically depends on the dry and wet deposition rates of gases and particles. The main components of the long range transport will be the fine particles ($< 2.5 \mu\text{m}$) and the less reactive gaseous components. In summer, an active vegetation, open water, and sun radiation will reduce the residence time in the atmosphere of both gases and particles, while in winter a lower temperature, darkness, and frozen, snow-covered ground will lead to much longer residence times at high latitudes. Chemical reactions, evaporation and adsorption deter-

mine the transfer of the specific chemical components between the gaseous and particulate fractions. Many stable organic components have a certain vapour pressure in the solid state and may therefore be re-emitted to the atmosphere after initial deposition. In such cases it will be important to specify more closely what is meant by "residence time".

Modeling of the long range transport of air pollutants involves a number of approximations, and the calculated concentrations are usually compared with 24 hourly point measurements at ground level, while concentration profiles measured from aircraft show that most of the transport takes place well above the ground. This limits the day-to-day agreement obtained between observed and calculated concentrations. Better agreement is usually obtained for mean values over extended periods of time. Principally, the same applies to mean values for larger areas. Measurements representative for the air over larger areas should therefore give better agreement. The simplest approach may be to use statistics on time series of observations from two or more stations in the area. Remote sensing, long path spectral absorption, and aircraft sampling over a larger area is also possible, but the complex techniques and the costs involved have so far prevented any extensive use of such methods in long range transport studies.

10 CONCLUSIONS

Research during the last decade has shown that air pollutants are distributed throughout the atmosphere. The main transport takes place within the lower 1 or 2 km of the troposphere, but some pollutants may even penetrate into the stratosphere. If the residence time in the atmosphere is sufficiently long, the pollutants contribute to the general global background composition of the atmosphere all over the globe, from the Arctic to the Antarctic.

The dispersion of pollutants is governed by the wind and other meteorological conditions. The large scale annual and seasonal

mean concentration patterns are closely related to the general circulation in the atmosphere, and the deposition in remote areas is highly influenced by precipitation.

The main inorganic components, such as sulphur dioxide, nitrogen oxides and particulates have been extensively studied in connection with the long range transport of air pollutants. The organic components are more difficult to measure and early evidence of their long range transport was mainly based on analyses of biological samples where an enrichment of the component had taken place. In recent years sampling techniques have become available which makes it possible to analyse both air and precipitation samples (Thrane and Mikalsen, 1980). The results have confirmed earlier observations.

As the sensitivity of the methods for sampling and analysis is improved, more and more components have been identified in connection with the long range transport of air pollutants. This applies to the inorganic as well as the organic components. Analyses show that the primary pollutants are accompanied by a number of secondary components formed during the transport. These secondary pollutants affect the oxidation rate of the sulphur dioxide and add to the acidity of the precipitation. They also have their own specific effects. This results in a rather complex interaction between gases and aerosols, whose composition depends on emissions along the pathway and the general conditions in the actual geographical region. However, the complex composition of the pollutants may also be used to identify their types of sources by analysing the clustering of the different components.

On a day-to-day basis, the smooth, long term concentration and deposition fields are distorted by short term fluctuations. Detailed analyses of these fluctuations are important in order to examine the physical parameters used in the transport models, and for the identification of source areas.

The long term ecological effects of the pollutants are mainly related to the mean values of deposition over a long period of time, while the short term fluctuations are more relevant for acute effects, such as haziness and vegetation damage due to exposure above a certain threshold. In most cases serious damage due to air pollution is limited to certain areas or regions. Cases where the damage has caused such changes that the situation will not revert to normal over a period of years without extensive remedial action, are generally limited to the vicinity of some large or particularly harmful sources. An example is the "moon landscape" found around some metal smelters due to the sulphur dioxide emissions.

Regarding the long range transport and world wide deposition of air pollutants, the possibility of irreversible changes in a long term perspective is of particular importance, because they may affect living conditions over large parts of the earth's surface. In some areas environmental changes have already taken place on such a large scale that nature has not been able to return to the original state by itself. One may mention deforestation, soil erosion and desertification. The acidification of the precipitation by air pollutants over the North American continent is by some characterized as a "national disaster". Still, the geographical scale of these disasters is limited, compared to the dimensions of the earth's surface, and timely actions may make it possible to improve the situation considerably, since, at least in theory, these changes are not irreversible.

A change in the climate would affect much larger areas, and from present knowledge it seems improbable that the situation would return to the situation we have today. An increase of the temperature in the Arctic of 3-5°C would lead to a melting of the Arctic ice cap (this would not change the water level, because the ice floats on the water). It would also lead to an increased absorption of solar radiation in summer, and if the carbon dioxide level was reduced, this might compensate for the reduction of the "greenhouse effect". Other changes which are more difficult to survey, may add to this irreversibility.

A different and perhaps more disastrous possibility is the contamination of our environment by chemicals which disturb the normal reproductive cycles of the living organisms. Nuclear warfare and an increased ionizing radiation level is frequently pointed out in this relation. Another possibility may be a wide spread introduction of persistent mutagenic and carcinogenic chemicals in our environment. Extremely low concentrations are required for some of these substances, and with the enormous production capacity of modern industry, a biological catastrophe could be imagined.

The polychlorinated hydrocarbons are particularly relevant in this connection. There is ample evidence that the reproduction of fish and birds has been seriously disturbed in areas where DDT and other chlorinated chemicals have been used in large amounts over a longer period of time. Based on this experience, the use of such substances has been severely restricted in many countries. Still, more than 500 000 tons of DDT and other chlorinated pesticides are used each year in tropical areas, and the World Health Organization claims that if this is stopped, a large increase of the malaria deaths would result. There are strong indications that these chemicals are not all broken down in the tropical areas, but that considerable amounts are slowly transported into the temperate and polar regions. To ascertain the extent of this transport and its future implications may perhaps be the most significant task in air pollution research at present.

In an evaluation of the future air pollutions research needs Hidy et al. (1979) came to the conclusion that the possibilities of a climatic change and the significance of the indiscriminate use of chemicals will be the two most important future problems in air pollution, because the effects are world-wide and may be truly irreversible. Considering the enormous production capacity of modern industry and the rapidly expanding consumption of an increasing human population, this development may seriously affect our natural environment, the basis of our existence. We may not have much more than 20 years in which to take the necessary steps to prevent such developments from running out of hand (WMO, 1981).

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