Report on the second informal conference on atmospheric chemistry, held at the Meteorological Institute, University of Stockholm, May 31—June 4, 1955

By ERIK ERIKSSON, Institute of Meteorology, University of Stockholm

Last year in May an informal conference in atmospheric chemistry was held at this Institute, a note on which was published in the third issue of Tellus for 1954. In this conference a number of scientists took part, representing studies such as meteorology, oceanography, geology and agriculture. The aim of the conference was to focus attention on the role played by the atmosphere in the circulation, transport and redistribution of certain chemical elements and the possible geochemical, meteorological and practical importance of such processes. It is necessary to establish observational networks in order to study these processes.

As a result of the conference a network of stations was established in the Scandinavian countries, for the collection of monthly air and precipitation samples. Shortly after the conference cooperation with Great Britain was arranged through Prof. P. A. Sheppard of Imperial College (London), which added five stations in England and Scotland. This was originally thought would serve as a link between the Scandinavian network and the United States—North Atlantic net planned by Dr. Chr. Junge from the Air Force Cambridge Research Centre, who also took part in the conference.

A separate network of stations for regular sampling of air for CO_2 was also an outcome of the conference, and this now covers the whole of Scandinavia. Both networks are in operation and the data are published regularly in this journal as a special bulletin.

The present conference was organized by Prof. C. G. Rossby from this Institute and Dr. H. Egnér from the Royal Agricultural College of Sweden, Uppsala, and was attended by the following invited foreign guests:

Dr. W. Bleeker, Koninklijk Nederlands Meteorologisch Instituut, De Bilt, Holland.
Dr. J. Bouquiaux, Institut d'Hygiène et d'Epidemiologie, Bruxelles, Belgium.
Prof. K. Buch, Oceanographic Institute, Helsingfors, Finland.
Dr. L. Facy, Météorologie Nationale, Paris, France.
Dr. J. Grandjean, Institut Royal Météorologique de Belgique, Bruxelles, Belgium.
Dr. Kurmies, Versuchsanstalt Thomasphosphat, Essen, Germany.
Dr. F. Koroleff, Oceanographic Institute, Helsingfors, Finland.
Dr. H. Riehm, Staatliche Landwirtschaftliche Forschungs- und Versuchsanstalt, Augustenberg near Karlsruhe, Germany.

The conference was attended also by Swedish representatives invited from various research institutions and organizations, representing agriculture, forestry, geology, medicine and technical sciences.

The following visitors at the Institute from abroad were also present during the conference:

Dr. J. Adem, Institute of Geophysics, University of Mexico, Mexico City.

Mr. E. Barrett, Woods Hole Oceanographic Institution, Woods Hole, U.S.A.

Mrs. C. Barrett, Institut Royal Météorologique de Belgique, Bruxelles, Belgium.

Mr. P. Bergthorsson, Icelandic Weather Service, Reykjavik, Iceland.

Lt. Col. W. Best, U.S.A.F. Weather Service.

Dr. A. P. Burger, South African Weather Bureau, Pretoria, S. Africa.

Mr. E. Charasch, Meteorological Service, Lod Airport, Israel.

Lt. Cdr. M. Eaton, Office of Naval Research, Washington, U.S.A.

Mr. J. Hughes, Office of Naval Research, Washington, U.S.A.

Lt. Cdr. Masterton, Office of Naval Research, Washington, U.S.A.

Mr. C. Ramaswamy, Weather Service of India, India.

Mr. P. M. Saunders, Imperial College, London, England.

Mr. H. Tabatabay, Iranian Weather Service, Tehran, Iran.

The conference was opened by Prof. C. G. Rossby, who in some introductory remarks outlined its purpose. This was ultimately to discuss and make recommendations on two important questions concerning future cooperative work, namely how to improve and extend the present network and how to maintain it. Before any measures are taken it is, however, necessary to make some kind of list of the various areas to which the results can be applied. After this list has been made the future organization of the network will be discussed. At present it seems reasonable to have the network extended so as to cover France, Belgium, the Netherlands, West Germany and probably Switzerland. The Mediterranean area is also important and an extension so far south is a future goal.

Prof. Rossby also mentioned that Dr. Junge's network will probably be ready this year and that it seems likely that it will be extended south by the cooperation of Dr. Fournier d'Albe, of the Institute of Geophysics, Mexico. It may also be possible to extend it north through cooperation with the Canadians. If all this can be achieved there will be a network for the study of the chemical climate which covers a large part of the northern hemisphere.

Dr. H. Egnér gave a brief outline of the history of the present European network, which dates back to 1945 when the early Swedish network was planned. He also mentioned briefly some practical details concerning the present network.

In the afternoon Prof. Buch discussed the background to the present CO_2 net in Scandinavia. Up to date there are 230 samples of air from this network analysed and the average CO_2-content of these is 3.36×10^{-4} atm. This value, compared with the data compiled by Callendar, indicates a linear increase since 1900. As to the distribution this is remarkable, as the bulk of values are fairly evenly distributed around the mean. A division of the data according to the classified air masses has also been made with the result that the 60 per cent of continental polar and 40 per cent of maritime polar air masses have the same mean value. Unfortunately, no arctic air masses were sampled. He pointed out, however, that the series is too short as yet to be representative.

Prof. Buch also discussed the recent paper by Dingle in Tellus on the rate of exchange of CO_2 between the air and the sea in the North Atlantic. Dingle has used for his calculations a constant value for the CO_2 pressure ($= 3.0 \times 10^{-4}$ atm.). As this pressure in fact, however, is generally considerably higher, one can presume that the CO_2 exchange atmosphere—sea in the northern regions is more rapid and the reverse exchange in the southern parts slower than appears from Dingle's calculations. Better knowledge of the CO_2 concentrations over the North Atlantic would be highly desirable.

Another point Prof. Buch made concerned the influence of combustion of fossil carbon on the C^{14} activity of very recent organic material. If no exchange of the carbon dioxide had occurred it should be revealed by a decrease in the C^{14} activity of the atmospheric CO_2 and indirectly also of the very recent plant material compared to the C^{14} activity of plant material formed 100 years ago.

In the discussion afterwards Dr. G. Arrhenius from the Scripps Oceanographic Institute mentioned that this matter has recently been investigated in USA but that no distinct differences were obtained.

Finally Prof. Buch mentioned the influence of an increase of carbon dioxide in the atmosphere on the heat economy of the earth. The greatest effect would occur in polar regions, where the amount of water vapor is low.

During the discussion Prof. L. G. Romell, from the Swedish Research Institute of Forestry, made some comments on the sampling of air for CO_2 analyses. He pointed out that it would be advisable, in work of the scope now under discussion, to take the samples 100 metres or more above the ground, avoiding the bottom layer of air which has a rapidly fluctuating CO_2 content owing to photosynthesis and soil respiration. Mr. Eriksson replied that the sampling was done at a time of the day when the turbulence in the air could be expected to be at its maximum. Also the sampling sites were chosen as far as possible on gravel grounds, roof tops, etc., where the influence of vegetation would be expected to be small. Further, a probably greater error is introduced during the late fall—early winter seasons, when an accumulation of CO_2 may take place below the rather frequent low inversions.

The last lecture this day was given by Dr. Facy, who reported on present work on atmospheric chemistry in France. He pointed out that the main work so far had been done from the cloud physics point of view, and was concerned therefore mainly with the particulate matter in the atmosphere—the so-called condensation nuclei. In Paris, however, routine investigations on the gases CO_2 and SO_2 are being carried out, and it appears that there is a marked positive correlation between them. The correlation differs in summer and winter, which can be accounted for by variations in industrial and social activities.

As to the particulate matter he described different methods for the collection and the study of these, including the use of the electron microscope. It has been found experimentally that repeated condensation and evaporation on giant nuclei will practically clean the air of very small particles by a mechanism very much like thermal precipitation. When condensation occurs the flux of water vapor towards the surface of the drops causes a flux of very small particles in the same direction. Once they are caught by the drop they will be included with the original condensation nuclei on subsequent evaporation.

As to the sea salt nuclei derived from spray, he mentioned some important observations made on these during evaporation. During slow evaporation a very few cubic crystals, presumably of sodium chloride, form in each drop. When the evaporation is rapid the crystallization occurs explosively, scattering the cubic crystals. In the electron microscope a great number of very small particles can also be seen to have formed, presumably consisting of calcium sulphate crystals in a magnesium chloride solution.

Dr. Facy also mentioned investigations on portions of rain during rainfalls, mainly showers. It was found that the very first portion of the rain contained very high concentrations of substances, especially of sodium chloride. The results also indicated that the last traces at a shower may give information on what was originally in the rain.

In the discussion afterwards Mr. Eriksson said that investigations on portions of rainfall carried out at this Institute in Stockholm did not give any pronounced decrease in concentration with time. The variations within a rainfall were quite large and the only thing which seemed to be reasonably constant was the rate of sodium deposition. The locations of sampling, however, are not comparable and may account for the difference in results.

The second day was devoted to subjects relevant to geochemistry and paleoclimatology. Mr. E. Eriksson from this Institute talked about the chemical composition of river waters in relation to airborne salts. (A paper on this subject is published in the second issue of Tellus 1955.)

Afterwards Dr. Egnér discussed the gaseous equilibria between air and water. He presented a table showing the various gases occurring in the atmosphere and showed on a graph the solubility of these under varying pH conditions. The pH greatly affects the solubility of gases which can form acids or bases in solution like hydrogen sulphide, sulphur dioxide, ammonia and carbon dioxide. The rate at which equilibrium is established varies greatly with the type of gas, being for instance very rapid for amonia and very slow for carbon dioxide.

The importance of these gases in the at-

mosphere to soils, plants, technical constructions and human beings has yet to be assessed. Once we know their amounts, variations and behaviour a good deal can be predicted.

In the afternoon Prof. S. Mattson from the Royal Agricultural College, Uppsala, gave some interesting details on the chemistry of a so-called raised bog in the south-west of Sweden. As such a bog is cut off from nutrient supply from below its growth and composition must reflect the temperature, humidity and chemical climate. Nutrients are supplied practically only from the air. There are many indications of varying climatic conditions since the glacial epoch in these bogs, and with aid of pollen analyses it is possible to date the material to some extent. As to the chemical constituents the common cations such as sodium, potassium, calcium and magnesium occur as fairly easily exchangeable ions and are therefore mobile in the bog. Others such as ammonia, phosphate, silica and aluminium oxide are fairly firmly fixed, especially ammonia, which is intimately bound in the organic matter. The yearly accumulation of such constituents may therefore be calculated and will reflect varying conditions in the chemical climate. As the dating is fairly approximate and can be done only at certain selected levels, the averages have some degree of uncertainty and represent rather long time periods. The most remarkable feature of the bog investigated by Prof. Mattson was that the rate of accumulation of nitrogen (presumably as ammonia) has been fairly constant during most of the time up to the last period when it increases remarkably, a fact which Prof. Mattson interpreted as being due to the increase of population and of domestic animals, and the industrial combustion of coal during the last centuries. He showed that if the increase was assumed to have taken place in the first 30 cm (from the surface), which may correspond to a few hundred years, the increase in nitrogen content is about five-fold. The same though much stronger is indicated by phosphate.

In the discussion Dr. O. Arrhenius pointed out the possibility that the increase in the top part of the bog was due to an accumulation by plant roots from below. Prof. Romell referred to the distribution of phosphorus in a typical heath profile and stressed the fact that the uppermost soil horizon, dominated by living organic matter, is quite generally a zone of accumulation, due to biological action. Mr. Eriksson showed some estimates of the amounts of ammonia released to the atmosphere by domestic animals and industrial activities over Själland, not very far from the bog and in the direction of frequent winds. According to these estimates the annual release of ammonia per unit area has increased by a factor of around six since 1780. Considering the order of magnitude of these estimates he thought that the increase in the top part of the bog could very well be accounted for as being due to an increased rate of delivery from Denmark. Prof. Mattson also pointed out that the increase in the top part of the bog was not only restricted to ammonia and phosphate. A proportional increase of aluminium and silica had also taken place and this could not be attributed to biological enrichment.

The next forenoon was devoted to discussion of practical applications of research in atmospheric chemistry. Dr. U. Trägårdh, Tekniska Högskolan, Stockholm, and member of the Swedish Corrosion Committee, discussed some problems in atmospheric corrosion. Generally, corrosion is much more severe in industrial than in rural areas and more severe in maritime than in continental climates. There is a conventional classification of the climate used in connection with corrosion but there is no close correlation between this classification and the degree of corrosion. The rate of corrosion also seems to vary with the season and with the prehistory of exposure of metal constructions.

Sulphur dioxide gas has been found to have a strong corrosive effect on metals and it is very much enhanced by the presence of particulate matter, especially coal dust.

In the discussion Dr. Facy stressed the importance of the humidity. In desert regions corrosion is no problem whereas in humid areas it may be very severe. The role of microorganisms in corrosion should also be looked into.

Mr. T. Berglund, Sandviken Steel Works, also mentioned the importance of humidity and especially formation of dew on steel constructions. In presence of dust particles

the formation of dew caused by fluctuating temperatures leads to severe corrosion.

Mr. O. Johansson, Royal Agricultural College of Sweden, Uppsala, described some investigations on sulphur compounds in the atmosphere near a slate burning plant. He had found a fairly rapid decrease of these sulphur compounds in the prevailing wind direction. At a distance of 10 km the concentration in the air and in precipitation were quite normal. Another interesting thing brought out by this investigation was the surprisingly high amounts of sulphur taken up by the soil directly from the air. This amount was about twice as large as that received by precipitation.

In the discussion afterwards Dr. Egnér pointed out that the direct transfer of atmospheric constituents to the soil and vegetations seems to be quite considerable. This can of course be expected considering the amount of air which must come into contact with plants and the ground. Estimates from the daily assimilation of CO_2 and transpiration shows that it must be of the order of 500 m^3 of air per m^2 surface and day. The importance of the direct transfer to the ground of chemical constituents has been brought out here in three lectures, namely for ammonia by Prof. Mattson, for chloride by Mr. Eriksson and now for sulphur by Mr. Johansson.

Two of the staff members of the Swedish Public Health Institute reviewed some problems relevant to atmospheric chemistry. Mr. C. E. Holmquist discussed briefly health problems and atmospheric pollution. There are some standards for the tolerable limits of pollutants in industrial plants. The tolerable limit for SO_2 has been set to 10 ppm. However, during a severe smog in London in 1952 it was estimated that 4,000 people were killed by the smog, yet the SO_2 concentration was never more than 1.5 ppm. Therefore tolerable limits for one constituent have no meaning as long as we do not know what role other constituents may play. There are probably many organic compounds which may be of interest. He also mentioned that there is at present no uniformity of sampling methods and gave as an example the measurements of dustiness, which is assessed by different, incomparable methods in different countries.

Mr. G. Sjöström mentioned some recent results of research on iodine in foodstuffs, soils and water, carried out by the Public Health Institute. He mentioned that endemic goitre is at present no problem in Sweden but that there were two areas in which it existed earlier, one on the Highland in the south of Sweden, and the other in the provinces of Dalecarlia, Gästrikland, Hälsingland and Ångermanland. The iodine content of some soil profiles indicated, however, a beginning iodine impoverishment of the top layers of cultivated soils. The atmosphere is generally supposed to be the main iodine source for soils and it would therefore be of interest also from the public health point of view to examine the iodine content of air and precipitation systematically.

In the discussion afterwards Mr. J. Hughes, Office of Naval Research, Washington D. C., mentioned the peculiar circumstances of atmospheric pollution in the Los Angeles Basin where very high ozone contents were found, contrary to what would be expected. As to the iodine. Mr, Eriksson mentioned that the source for iodine in air is most probably the sea and that the iodine chloride ratio in rainwater is much higher than that in sea water. The chemistry of iodine is also more complex than that of chloride. Dr. Egnér asked whether the content of nitrous oxide (laughing gas) and presumably its geographic distribution could have any effect on the behavior of human beings. To this Mr. Holmquist answered that he did not know of any investigations on this.

The afternoon was devoted to a meeting on the European network of stations for air and precipitation samples. Prof. Rossby opened this session by summarizing the preceding events. It seems obvious that the results of synoptic air and precipitation analyses have a very wide application and there is no doubt that an improved and extended network in Europe would give valuable and detailed information over a considerable area. Prior to this conference representatives from France, Belgium, the Netherlands and Germany have expressed their interest in the present network and suggested additional sampling points in their countries. The first step to take now is therefore to make a first decision on the number and position of additional sampling points. As the analytical burden of the Royal

Agricultural College in Sweden cannot be increased further, the future arrangement of the analytical work has also to be decided upon.

As to the analytical data received from the new network, Prof. Rossby suggested that they should be published in the same way as at present, namely quarterly as a special bulletin in Tellus.

Prof. Rossby also gave some information on the financial side of the network. The cost of equipment is about 700 Sw. Krs. per station. To this should be added the cost of necessary electric installations. The operators of the stations in Sweden receive 200 Sw. Krs. yearly, and the present cost of maintenance of the whole net of 50 stations, including the cost of analyses and inspection travels, does not exceed 40,000 Sw. Krs. a year.

Dr. Facy discussed the situation in France. The Meteorological Service in France can set up sxi stations now, and as suitable locations he suggested Rostrenem, Le Mans, Bourges and Ambérieu roughly on a WNW—ESE line and Magny-les Hameaux and Luxeuil to the north of Bourges and Ambérieu respectively.Dr. Facy also mentioned that the Department of Agriculture may become interested and extend the number of stations in France so as to have southern France also represented.

As to Belgium, Dr. Grandjean stated that the Royal Meteorological Institute was willing to set up four stations, namely in Botrange, Dourbes, Uccle and one coastal station which has not yet been chosen.

Finally, Dr. Bleeker representing the Meteorological Service of the Netherlands, suggested that one, and possibly two stations, could be set up in the Netherlands, namely in Witteven, where a magnetic observatory is located (possibly one also in De Bilt). He was not certain, however, in what degree a sampling station in De Bilt would suffer from industrial contamination from the nearby city of Utrecht.

In Germany the number of stations and their position will be worked out later by Dr. Riehm and Dr. Flohn of the Meteorological Service in Germany. Dr. Riehm mentioned that six or seven stations may be established in West Germany. At present there are three planned: two around Feldberg in Baden and one at Augustenberg, near Karlsruhe.

As to the improvements of the network Prof. Rossby mentioned that the number of stations in Norway certainly will be increased, as this is a rather important region. In Britain also the number of stations will be increased and Prof. Sheppard at the Imperial College is at present trying to arrange for the analytical work for these stations to be carried out there.

Prof. Buch mentioned that the number of stations in Finland will be increased, making a total of about ten and that Dr. F. Koroleff will be ready to take over the analytical work for this area on July 1, 1956.

Concerning the analytical work from the remainder of the stations, Dr. Bouquiaux from the Public Health Institute in Bruxelles stated that analyses from about ten stations could be undertaken at his Institute. Prof. Rossby therefore suggested that the French, Belgian and Netherlands samples be analysed at Dr. Bouquiaux's institute, an arrangement to which the representatives for these countries agreed.

The analyses from the German net will be taken care of by Dr. Riehm. He thought it possible to manage samples from about ten stations and suggested therefore that samples which may be collected in Switzerland in future also be analysed in his laboratory.

By this arrangement of analyses centers Sweden can handle the remainder of the net, including additional points in Norway.

The extension of the CO_2 net was also discussed. Dr. Facy suggested Brest in France as a suitable sampling place, the analyses being made in Paris. In Belgium and the Netherlands additional sampling points are available and the analyses can be done at the Public Health Institute in Bruxelles.

Dr. Bleeker discussed some recent measurements of artificial radioactivity in air samples which are being taken on a routine basis in the Netherlands. He described the sampling method and mentioned some very interesting results. He stressed that such measurements are of immediate importance for human welfare and that the undue secrecy around such measurements should be removed. This would facilitate cooperative work on a large scale. Prof. Rossby suggested that this im-

portant question should be taken up for discussion in a letter to the editor of Tellus.

Lt. Col. W. Best, USAF Weather Service, who was not present during this meeting, had given the following information which he wanted made known to those taking part in the conference. The USAF Weather Service make routine weather reconnaissance flights over fixed routes in the northern hemisphere. These aircraft carry weather observing instruments and may well be capable, should the requirement arise, of carrying equipment for both sampling of chemical constituents in the air and for direct measurements of those constituents during flight.

On the last day of the conference, at the Royal Agricultural College of Uppsala, the forenoon was devoted to lectures and discussions. Prof. Rossby discussed some recent results of a study of the chloride to sodium ratio in precipitation in Sweden, as related to the mean monthly circulations (paper by Rossby and Egnér published in the first issue of Tellus 1955).

He mentioned among other things that the yearly variations in the amounts of various constituents is intimately connected to the general circulation and is a much more sensitive indication of circulation changes than for instance temperature and rainfall. He showed that 1949 had very much higher sodium values than later years and that the circulation that year was distinctly characterized by west winds whereas in later years the mean pressure charts show a great deal of continental influence.

In the discussion afterwards Mr. Thuresson from the Becker Co. Paint & Laquer Industry mentioned that 1949 was a rather severe year for corrosion of paints on wood compared to later years. Mr. T. Berglund from the Sandviken Steel Works said that he too had had the same experience concerning steel corrosion.

Mr. Barrett reviewed a recent paper which he had prepared with Mr. G. Brodin of the Royal Agricultural College on the pH in precipitation (to be published in the second issue of Tellus 1955). The pH values at coastal stations are generally on the acid side and are frequently as low as 4.8 on the west coast. Inland the pH values are as a rule on the alkaline side (compared with distilled water in equilibrium with atmospheric carbon dioxide). He also discussed possible explanations for the low coastal values and suggested that H_2S liberated from sea water is oxidized to SO_3 and taken up by the precipitation. He suggested that ozone played a great role in this oxidation.

Mr. Eriksson made some remarks on possible mechanisms for the chemical separation of chloride from sea salt nuclei. Only one such process has been suggested so far, that proposed by Cauer, who thought that ozone in the air might oxidize chloride to chlorine, thus releasing it from sea salt spray. From known data this oxidation seems far too slow to be of any importance. Another process suggested by Mr. Eriksson is that SO_3 when being formed from SO_2 by oxidation is immediately taken up by the condensation nuclei in the air. As H_2SO_4 is formed the pH will drop sufficiently to cause an appreciable vapor tension of HCl (when chloride is present in the nuclei), as indicated by thermodynamic data. As the accumulation of SO_3 will be more important for small nuclei these will be more rapidly depleted of Cl than larger nuclei. The same mechanism is likely to operate in presence of HNO_3 in the air instead of SO_3. As H_2SO_4 is less volatile than HNO_3 and this is less volatile than HCl, HNO_3 will operate mainly on the largest condensation nuclei when both SO_3 and HNO_3 are present.

In the discussion Dr. Bouquiaux doubted that the open sea could be any source for H_2S in the air as the oxygen supply in the sea is ample. He thought, however, that a considerable quantity can come from the part of the sea bottom which is exposed by tidal fluctuations. Mr. Eriksson mentioned that the Hawaian rains also were fairly acid, apparently due to an addition of SO_2 which can hardly be of continental origin.

The afternoon was devoted to demonstrations by Dr. Egnér and Mr. Brodin of the equipment used for sampling air and precipitation in the present network, and of the laboratory used for the analytical work. After this demonstration a sight-seeing tour through Uppsala followed, and the conference was closed by a dinner party at the Royal Agricultural College.