The Fourth Annual Conference in Atmospheric Chemistry May 20—22, 1957

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The fourth in a series of informal conferences on atmospheric chemistry was held at the International Meteorological Institute in Stockholm, May 20—22, 1957.

The first two days were devoted to lectures and discussions at the Institute in Stockholm, whereas the third day was traditionally spent at the Royal Agricultural College in Ultuna.

The conference was attended by the following representatives.

A. P. Baez, Mexico
L. D. Baver, Hawaii
W. Bleeker, Netherlands
B. Bolin, Sweden
J. Bouquiaux, Belgium
G. Brodin, Sweden
K. Buch, Finland
L. K. Coachman, Norway
W. Dansgaard, Denmark
D. Djurić, Yugoslavia
B. R. Döös, Sweden
M. Eaton, U.S.A.
H. Egnér, Sweden
T. Enns, Norway
E. Eriksson, Sweden
S. Fonselius, Sweden
E. M. Fournier d'Albe, Mexico
J. Grandjean, Belgium
K. Groth, Sweden
Edw. Hemmingsen, Norway
B. Holma, Sweden
Ed. Jess, U.S.A.
O. Johansson, Sweden
Chr. Junge, U.S.A.
F. Koroleff, Finland
O. Lang-Rasmussen, Denmark
S. K. Love, U.S.A.
J. Låg, Norway
W. Mordy, U.S.A.
G. Neumann, Sweden
B. C. V. Oddie, England
C. Rooth, Sweden
E. Schmacke, Sweden
P. Scholander, Norway
B. Torsell, Sweden
S. Williams, U.S.A.
A. Wiin-Nielsen, Denmark
G. Witt, Sweden

In some introductory remarks it was pointed out by Mr. Erik Eriksson that there had been a considerable expansion of the general field of atmospheric chemistry since the first conference, held in 1954. New topics have been included in the field and it is no longer possible to cover the whole field in a small conference of the present make up. Hence those subjects which are of greatest common interest have to be favoured in the program.

For tracing and recognizing the paths of various compounds through the atmosphere, isotope-techniques have gained increasing importance during the last few years. Consequently several lectures will be devoted to the application of isotope studies.

Another topic of major importance concerns surface films, their properties and possible geochemical significance.

The first day of the conference was devoted primarily to subjects concerning the CO_2-

content in the atmosphere. This series of lectures was begun by Dr. Bolin, who gave a general survey of the CO_2-circulation in nature.

It is possible at present to give a rather complete picture of this circulation between the different natural reservoirs of carbon dioxide. By the work of several investigators (Craig, Revelle & Suess, Arnold & Anderson, Tellus 9: 1 pp. 1—32 1957) the possibility of quantitative estimates of exchange rates using radiocarbon data has been demonstrated. Especially remarkable is the good agreement for the half-life of CO_2 in the transport between the atmosphere and the upper part of the sea (the so called mixed layer) obtained by different workers.

It would, however, be of great importance to know more about the CO_2-transport between the mixed layer and the deep sea. Dr. Bolin concluded by suggesting the following four topics to be subjected to more intensive research.

1) Determinations of C^{14} in the ocean and especially in the mixed layer.
2) Simultaneous measurements of CO_2 in the sea and in the atmosphere.
3) Carbon dioxide measurements in the free atmosphere.
4) Measurements in critical regions (Polar-regions and the Equator).

In the discussion following this general survey the interest was concentrated around questions of the general circulation of CO_2, the C^{14}-dilution process by combustion of fossil carbon (the "Suess effect") and on the representativity of the CO_2-data from the Scandinavian network.

Dr. Christian E. Junge pointed out that the average time for the transport of CO_2 from the stratosphere to the troposphere is probably of the same order as the corresponding figure for the transport from the atmosphere to the mixed layer (10 years according to Revelle & Suess).

On a question of Dr. E. M. Fournier d'Albe, Mr. S. Fonselius said that there has not been observed any systematic seasonal variations in the Scandinavian CO_2-data.

In a short lecture Mr. Erik Eriksson gave a brief account on some CO_2-measurements he had made during a cruise on board the Soviet icebreaker "Ob" in the sea between Spitzbergen and Greenland. The air samples taken in this area, partly covered with drift-ice, showed rather high CO_2-values but with considerable variations. He thought that the explanation for this is the slow exchange with sea water of descending CO_2-rich air, probably of tropical origin.

In another short paper Mr. S. Fonselius showed some CO_2-data recently obtained from air samples taken on a voyage from Montevideo to Stockholm. It was remarkable that these data fitted very well into the pattern of the CO_2 partial pressure in the ocean at 100 m depth obtained during the "Meteor"-expedition in 1927—28. This indicates that the upwelling regions are important sources for CO_2 in the atmosphere.

Mr. W. Bischof described some flights (both with propeller-plane and with glider) which he had undertaken to obtain CO_2-analyses of air sampled from air planes. Data from the Mälar-district west of Stockholm and from Åre in the north showed large variations both with time and altitude.

The possibility of obtaining information on past atmospheric compositions was demonstrated by Mr. L. K. Coachman, who presented some figures on the composition of glacier-ice gas enclosures. As both nitrogen and argon can be regarded as strictly conservative, the expected composition with respect to oxygen and carbon dioxide can be computed and compared to actual data. He showed that for Greenland glacier ice the oxygen content of the enclosed air was close to that expected, but for CO_2 the analyses were scattered around a value nearly twice as high as at present. This could be due to a different composition of air with respect to CO_2 in the past. The technique used in the determinations was illustrated by an excellent colour film.

In connection with this work Mr. Edward Hemmingsen described some measurements of CO_2- and O_2-diffusion through ice. The rate constants obtained were very low, thus excluding the possibility of gas escape from ice-enclosures. Furthermore Mr. Hemmingsen described a technique for sampling CO_2 from enclosed air in glacier ice in quantities large enough for C^{14} dating. The technique is ingenious and simple, though

necessarily time consuming. At least five cubic meters of ice have to be melted and extracted.

The next session was devoted to surface films. Mr. C. Rooth gave an orientation of theoretical questions involved under both idealized conditions and field conditions. He pointed out that surface active agents present on cloud droplets could have some influence on the rate of evaporation from these.

Mr. K. Groth gave a brief survey of the surface chemistry of long chain alcohols and acids and showed some practical results he had obtained in field experiments on evaporation control by spreading mixtures of cetyl alcohol and red iron oxide on snow surfaces.

The possible effect of surface films on the coalescence of cloud droplets was discussed by Mr. W. A. Mordy. He described some experimental arrangements for studying the process of coalescence of droplets as a function of size and relative velocity. The experiments were illustrated by an interesting film taken by means of a high speed camera at a rate of 3,000 frames per second, showing the process of collision between different droplets. It was obvious from the film that the simple Langmuir theory cannot account for the observed processes. The presence of surface films in some examples was apparently related to elastic bounces of the colliding droplets. In the discussion possible electric effects were also mentioned.

In the next paper Mr. G. H. Neumann drew attention to the fact that the content of organic matter in precipitation frequently amounts to about 50 % of the total solid content. There are great difficulties involved in the determination of the total organic carbon present but it has been possible to develop a few relative micro-methods based on the consumption of suitable oxidizing agents under standardized conditions. Even ultraviolet absorbtion spectra from precipitation samples gave some interesting results. Mr. Neumann concluded his talk by showing some results obtained from the Scandinavian network and some data from micro-elementary analysis of snow samples.

In the discussion that followed Professor J. Låg remarked that the elementary analyses indicated that humic substances were important organic constituents in precipitation. Mr. Eriksson agreed upon this and said that the ultraviolet spectra supported this conclusion.

The second day of the conference was partly devoted to a review concerning atmospheric chemical networks. Of special interest were some reported extensions of the present European network. If possible, stations in South-Eastern Europe will be incorporated. The conference even got reports about some new stations in Belgian Congo.

Dr. E. M. Fournier d'Albe mentioned that there are plans to develop a rather extended network in Mexico. The topography of the country makes it possible to make studies of the variation of the chemical climate with altitude. In spite of difficulties in organization four sampling stations are now in operation.

Dr. Fournier d'Albe also mentioned that the Mexican stations will possibly be equipped with an automatic rainwater collector which permits to collect fractions of a single shower. This will be of great interest from the cloud physics point of view. Concerning this later subject Dr. Fournier d'Albe discussed the theoretical possibilities of studying the mechanism of NaCl-cloud seeding by observing changes of the Cl/Na-ratios in artificially initiated showers.

The American network plans were discussed by Dr. S. K. Love. He emphasized that much would be gained by a critical review of many analytical methods now used by various networks. There is surely still a great risk that some of the data obtained may be unreliable, in spite of the representative sampling. He also recommended that different network organizations have their own analytical laboratories instead of depending upon analyses made by commercial companies.

Speaking of plans for a network which could succeed the US Air Force network formerly organized by Dr. Junge, Dr. Love said that there were preliminary plans for running a limited US network during the IGY. Furthermore there are plans for a world-wide investigation of dissolved matter carried by surface streams to the sea. This investigation should comprize about 65 of the most important rivers in the world, and Dr. Love mentioned that it would be enough to take four samples per year from every river.

The analyses will be carried out in the United States or, if facilities are available, also in other countries. Because of the short preparatory time available these investigations will probably just get started during the IGY, but should then be continued at least for another year.

In connection with this Dr. Bolin mentioned the possible importance of direct ground water transport of dissolved material from land to sea.

The next session was concerned with isotopes in atmospheric chemistry. Three papers were devoted to this topic.

Professor W. Bleeker gave an account on the organizational work hitherto done in order to set up a network for regional radioactivity measurements. The working group, selected at the radioactivity conference in Brussels last year, made some preliminary recommendations at the meeting in Utrecht in January this year. Air filtration samples should be taken in 24-hour periods using a uniform method described in a manual by the working group. For a world-wide network, a density of one sampling station in every 10^5 km^2 is recommended. It would be of great value to coordinate the radioactivity determinations with radiosondings. Besides measurements of the total natural radioactivity, special samples should be taken for determination of fission products such as Sr^{90} and Cs^{137}. For tracing air masses in general and determining vertical mixing ratios and particle storage times there is also need for radioactivity measurements. Finally Professor Bleeker pointed out the possibility of determining the "preatomic" tritium content in air from ice-samples.

Dr. Bolin mentioned in the discussion that there had been recommendations on total fallout networks of the same density. The latitudinal distribution of radioactivity would be most interesting from a meteorological point of view as it should give some hint on where the essential mixing between stratosphere and troposphere takes place.

A second contribution to the isotope-discussion was made by Dr. W. Dansgaard who had made mass-spectrometric studies of the O^{18} content of different natural waters. There was much evidence for a "distillation column" effect in atmospheric evaporation and condensation. This effect seems to result in a correlation between the yearly mean temperature and the O^{18} content of fresh water in a geographical region. With this relation it would be possible to study past climatic conditions by analysing O^{18} in glacier ice of known age.

Finally Mr. E. Eriksson discussed the use of tritium in the study of the hydrological cycle. With a paper by Begemann & Libby (1956) as a starting point, Mr. Eriksson showed that with a more refined model of the circulation of water than that of Begemann & Libby, quite different results are arrived at. The estimated ground water storage becomes much less than in their case and their assumption about a short residence time of tritium in the stratosphere can be questioned.—Their assumption about rapid mixing of ground water seems to be unsatisfactory and may lead to unlikely results. An empirical method based upon tritium determinations in river water for obtaining the time characteristics of ground water basins was suggested.

On the last day of the conference Dr. Christian E. Junge discussed results obtained from the US Air Force precipitation-sampling network. An impressive amount of work has been done in collecting data from 63 stations involved in the network. The character of this network was rather different from that in Scandinavia, not only with respect to the lower density of stations in the United States, but also with respect to the careful precautions taken by Dr. Junge to prevent atmospheric dust and dry fall-out to mix with the precipitation samples. Dr. Junge showed the regional distribution of various inorganic ions. The data involved the same ions as the Scandinavian current data. Dr. Junge made some interesting remarks on the Cl/Na ratio in precipitation. In all inland stations this ratio was considerably smaller than the corresponding value in sea water. The same phenomenon was much discussed in connection with the analysis of the Scandinavian data. Dr. Junge thought it rather unlikely that this effect was due to a depletion of chloride from the precipitation. The other possibility would thus be an addition of sodium. But this could not probably be effected by sodium contamination from continental sources. According to Dr. Junge there might perhaps be an addition of

extra-terrestrial sodium from the stratosphere. There was no direct evidence against such a hypothesis. Finally Dr. Junge described some laboratory experiments showing the formation of ammonium sulphate aerosols from gaseous ammonia, sulphur dioxide and water at different pH.—Such a process could be responsible for the formation of a "London fog".

In the discussion Mr. Eriksson pointed out that addition of such amounts of extra terrestrial sodium are not compatible with the geochemistry of the sea. There are already difficulties involved in explaining the great excess of sodium in river waters after subtraction of "cyclic" sodium based upon the chloride-content in river water, unless one considers a separation of Cl from sea salts in the free atmosphere. There are likely processes that can well explain this separation.

Mr. G. Brodin concluded the series of papers by reporting some preliminary results obtained by him from analyses of precipitation for iodine, phosphorus and boron. These three elements are present in lower amounts than the elements hitherto considered. It is therefore necessary to apply certain micro-methods in the determinations. In spite of great technical difficulties the work will be continued, especially because of the medical and agricultural importance of these minor elements in the atmosphere.

In the evening the participants of the conference were guests at a dinner party given by the Agricultural College in Ultuna.