

4th December 1971

LONG RANGE TRANSPORT OF AIR POLLUTANTS
INFORMATION CIRCULAR NUMBER 1

This is a brief information review of the latest developments concerning the administration and technical status of the OECD project. It is intended to distribute such circulars about every 2 months in order to maintain an exchange of views and experiences of mutual interest as long as this programme is running.

Two copies are sent to the national representatives who are asked forward copies or extracts to the institutions or individuals engaged in the project.

ADMINISTRATION.

On September 29th the project plan was discussed in the Environment Committee of the OECD and unanimously recommended for implementation. The plan has now been forwarded to the OECD Council for final approval by the Member countries. The Council meeting is expected to take place in the near future.

NORDFORSK, which is an association of the National Research Councils in the Scandinavian countries, will continue its financial support of the development work for the project which is going on in the Scandinavian countries.

As soon as the mandate for the Steering committee of the project is decided by the OECD Council, the first meeting of the Steering Committee will be convened, probably early in 1972.

This means that there is not much time left in which to complete the preparation for the meeting of the Steering Committee.

At this meeting the results from the preparatory work in 1971 will be presented to give the Steering Committee a survey of the technical status of the project. To make this survey as up to date as possible, it is important that the countries send in their replies to the questionnaires 7/71 and 8/71 at their earliest convenience. As soon as this information concerning the equipment is received, a survey report will be worked out at NILU.

The sampling and analysis procedures which were partly covered in the descriptions (LRTAP 2-6/71) sent out by NILU the 16th of

September 1971 will be rewritten before the meeting of the Steering Committee so as to form a basis for the Committee's decision. Comments and criticisms to the LRTAP 2-6/71 papers (some have already been received) will be helpful in the preparation of these documents.

EMISSION FROM STATIONARY SOURCES

Data collected at OECD from the "Joint Group on Air Pollution from Fuel Combustion in Stationary Sources " have been used to obtain a survey of SO₂ emissions in (Western) Europe. This survey is based on the SO₂ emissions from the administrative districts within the respective countries, to the extent that these data are available, and supplemented by data for population density.

Mr Dehove was temporarily engaged by OECD for the preparation of this survey, and a first and preliminary emission model has been passed over to the data evaluation group. Further refinements of this survey are under preparation.

At the meeting of the "Joint Group on Air Pollution from Fuel Combustion in Stationary Sources" in Paris, 1-3 December 1971, an emission model was presented which is based on fuel consumption data and SO₂ emission source data in a square grid system. This model takes account of the variation of fuel consumption with ambient air temperatures. Fuel consumption for heating purposes is assumed to be proportional to the temperature decrease below 18° Evaluation of the model for a given situation can be carried out by means of a SIMULA computer programme.

DATA EVALUATION

The data evaluation group at the Norwegian Meteorological Institute has prepared a number of computer programmes to be used for data evaluation in 1972.

A programme is available which selects the necessary meteorological data from the regular WMO network, gives the wind speeds and directions as well as other met. data in a grid system for Western Europe every 6 hours. Another computer programme calculates the wind trajectories.

Models using these data and emission data to calculate the transport of air pollutants such as sulphur dioxide and sulphuric acid are under development.

During the period November 15th to December 20th daily forecasts of wind trajectories were obtained from the Swedish Meteorological and hydrological Institute and used in order to alert the Swedish Sampling Aircraft. Situations of special interest did not develop during this period.

GROUND STATIONS

most of the countries which have given answers to LRTAP 7/71 and 8/71 will be ready to start sampling at from 2 to 6 locations in January or February 1971. Sweden and Norway have been sampling since October this year.

Judging from the answers to the questionnaires more advanced sampling and analysis equipment is available than was originally assumed. A weak point in the sampling equipment, however, is the lack of satisfactory filter holders. It is essential that the filter holder should not retain sulphur dioxide by absorption, nor should it absorb particles by electrostatic attraction. Exposed brass or aluminium surfaces should be avoided or given a coating of solid paraffin or a varnish. Gold plating could also be used. The filter holder of hard polyethylene used by NILU has been found to be satisfactory with respect to SO₂ absorption and can be mass produced at a very reasonable price. It is still not perfect in all respects, however. Electrostatic effects have not been studied sufficiently and at present this filter holder cannot be used with cellulose ester (Millipore) membrane filters.

Development of more sophisticated intermittent air sampling apparatus is in progress. The air sampling device demonstrated by Dr Morkowski in Paris in June 1971 has been further developed after extensive testing at EMPA in Zurich, and units are now being tested at IVL in Sweden and at NILU. Similar equipment is also under construction at NILU.

The air intake specifications recommended in LRTAP 7/71 are designed

to give an effective cutoff at 10 microns. Particles larger than a few microns in diameter are not normally expected to be of importance in long range transportation, but this possibility cannot be excluded under special meteorological circumstances.

Representative sampling of the larger particles irrespective of wind speed and direction is a more complicated task.

At IVL Professor Brosset has been making comparative measurements with fixed and rotating sonds with respect to sampling efficiencies for different size fractions and will extend this work to experiments with a "ring slot sond" of the Walter design.

A ring slot sond with provision for size fractionation by a pre-filter cyclone is under construction at EMPA and will also be a contribution to solve this problem.

A sequential precipitation sampler has been developed by Dr Morkowski. One such unit has been ordered by NILU for testing this spring.

AIRPLANE SAMPLING

This has been given top priority both at IMI in Stockholm and at NILU. A complete sampling equipment has been developed at IMI and installed in the Swedish aircraft. Similar equipment, but with a large Venturi tube instead of an electric pump is under installation in a Norwegian aircraft. Comparative testing will take place in the near future. The capacity of the equipment is 1000 liter of air per minute through the filter and 200 l of air/min through the wash bottle. An absorption volume at 100 ml 0.3 % hydrogen peroxide is used. Sampling time is 10 minutes and SO₂ converted to sulfate is determined (after concentration by evaporation) by the Thorin method.

CHEMICAL ANALYSIS

Titration of strong acid

The procedure given in LRTAP-5/71 which involves a coulometric generation of OH⁻-ions has been used on a routine basis at NILU for about 3 months and has been found to give consistent results. The coulometric generation may of course be substituted with a volumetric addition of NaOH, the essential point is that a straight line should be obtained by Grans plot. A detailed review of the theory of the method worked out at IYL is enclosed.

Determination of sulphur dioxide.

It was mentioned earlier that when samples stored in polyethylene bottles were kept for long time or exposed to direct sunlight, an apparent increase of the sulphate concentration was taking place. This effect can be overcome by adding 1 ml of acetone to the absorption bottle before adding the hydrogen peroxide solution.

Attention is also called to the use of mixed-bed exchange cartridges for the production of deionised water. Sulphonic acids may be liberated from the resin and later decomposed to sulfuric acid. This effect can be particularly serious when evaporation of the sample solutions are carried out in order to detect very low concentrations of sulphate.

In this case it is probably wiser to use doubly distilled water from an all-glass still and pass the concentrated sample through a cation exchange column just before the spectrophotometric determination with barium perchlorate and thiorin.

X-RAY FLUORESCENCE DETERMINATION OF PARTICULATE SULPHUR ON FILTERS

Choice of filters

It has been recommended that Whatman no 40 filter papers should be used in the first and pilot phase of this study. This filter is closely similar to Whatman 1 with respect to flow resistance and can easily be used in existing sampling apparatus (OECD 1964)

Because it may later prove advantageous to use other filters, no unnecessary large numbers of Wh 40 filters should be purchased by the participants at this stage.

It is also recommended that new sampling equipment, (pumps and filterholders), should be selected with the possibility of using other filter materials in mind. Some data for flow resistances of various filter materials are enclosed.

A number of alternative filter materials have been tested, particularly with respect to XRF background counting rates, and variations in this background. Comparison of background variation expressed in $\mu\text{g S/cm}^2$ gives as the result that Whatman no 40 and

41-42) permits the detection of lower concentrations of particulate sulphur than any of the other filters tested.

Millipore membrane filters were acceptable, but introduce certain other difficulties (electrostatic effects and difficult handling). This filter material is not considered a practical alternative at the present stage.

X-ray fluorescence measurements

Because of the absorption of X-rays by the filter material, the penetration depth into the filters of a particulate sample will affect the measured fluorescence intensity. The penetration depth depends on flow rate, character and particle size distribution of the dust, and loading of the filter.

For the same reason, preparation of adequate filter standards for calibration is difficult. With the use of homogeneously impregnated filter paper standards prepared according to LRTAP 6/71 a set of easily reproducible secondary standards are obtained which would be helpful in reducing interlaboratory discrepancies. It is hoped that the values obtained in this way will not differ substantially from the absolute values, or that they will be related to the absolute values by a multiplication factor.

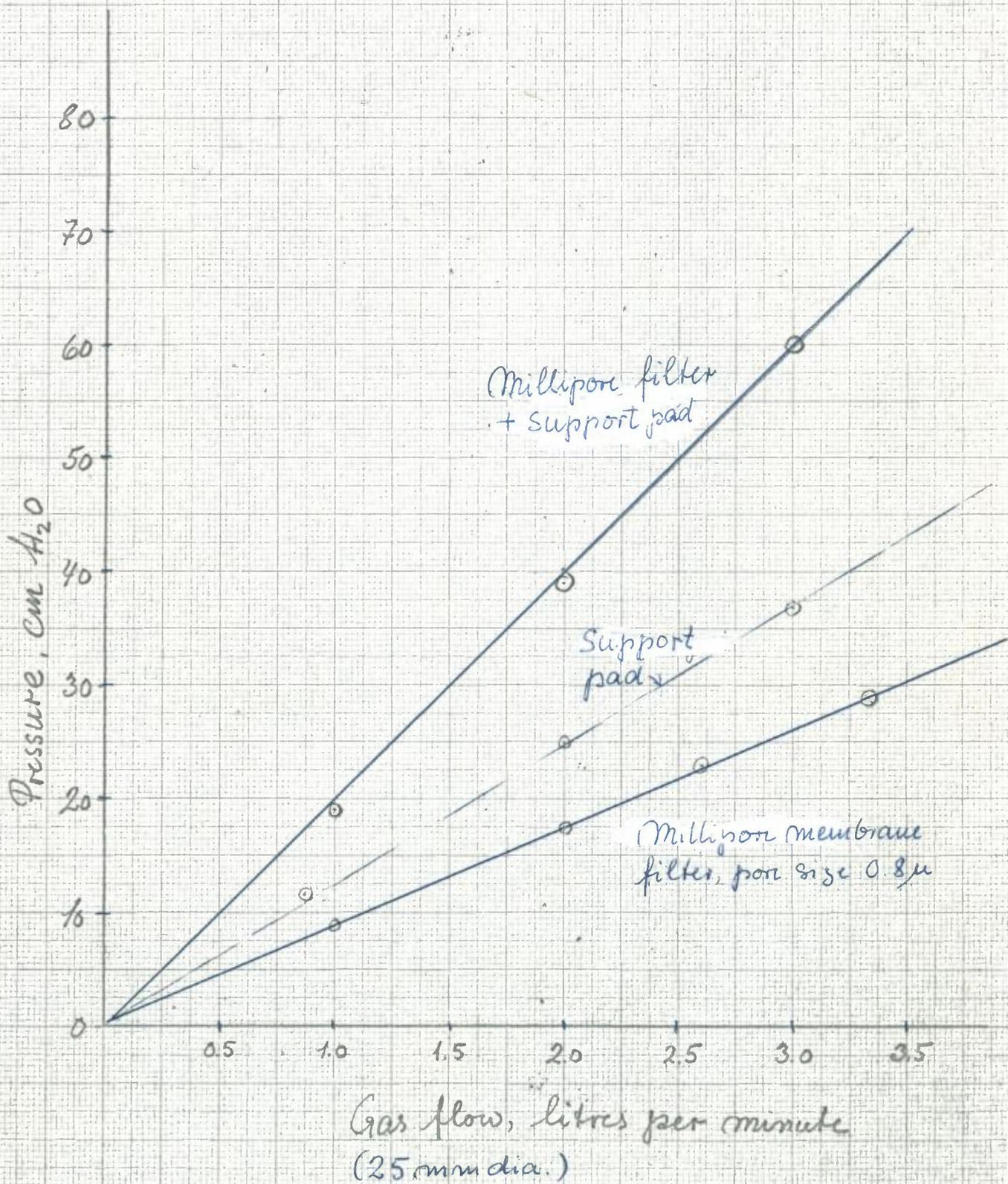
At the moment comparative testing involving air sampling on Wh 40 and Millipore membrane filters, is being carried out at IVL and NILU. More detailed information on recommended analytical procedures will be distributed when the results from these tests are available.

The Norwegian Institute for Air Research would like to thank the participants for their cooperation in the preparatory work for this project in 1971 and to wish everyone a Merry Christmas and a happy New Year.


B Ottar

Kjeller, 23th December 1971

We regret to say that Professor Brosset's report on the titration of strong acidity has been held up in the mail from Sweden. It will be forwarded to you as soon as possible



Pressure versus flow rates -
Whatman paper filters

