

NILU
TEKNISK RAPPORT NR: 5/83
REFERANSE: 20275
DATO: MAI 1983

EXPERIENCE AND FUTURE PERSPECTIVES
OF THE NMR EXPERT GROUP ON AIR
POLLUTION MEASUREMENTS 1975-82

BY
B. OTTAR

NORWEGIAN INSTITUTE FOR AIR RESEARCH
P.O.BOX 130, N-2001 LILLESTRØM
NORWAY

ISBN-82-7247-397-6

CONTENT

	Page
1 INTRODUCTION	5
2 RESULTS AND CONCLUSIONS FROM THE NMR-PROGRAMME ...	7
2.1 Measuring low concentrations of sulphur dioxide	7
2.2 Measuring low concentrations of nitrogen compounds	9
2.2.1 The nitrogen oxides	9
2.2.2 Ammonia	11
2.2.3 Gaseous nitric acid	11
2.2.4 Conclusions	12
2.3 Fractionated sampling of aerosols	12
2.4 The long range transport of micro-pollutants	15
2.4.1 Trace elements in aerosols	16
2.4.2 Elementary carbon	17
2.4.3 Organic components	18
2.5 The measurements systems	20
2.5.1 The Nordic background station network	20
2.5.2 Precipitation measurements	21
2.5.3 The representativity of ground stations	22
2.5.4 Aircraft measurements	23
2.5.5 Co-ordinated publication of Nordic environ- mental data	25
2.6 Long range transport modelling	26
2.6.1 The emission surveys	26
2.6.2 Atmospheric transport modelling	28
3 FUTURE ASPECTS	29
4 REFERENCES	33

EXPERIENCE AND FUTURE PERSPECTIVES OF THE NMR EXPERT GROUP
ON AIR POLLUTION MEASUREMENTS 1975-82

1 INTRODUCTION

In the summer of 1975 an expert group for air pollution measurements was established by the Nordic Ministerial Council (NMR) with the task to develop methods for a cooperative programme to monitor and evaluate the long range transport of air pollution in Europe (EMEP). The OECD/LRTAP project (1972-77) had shown that large amounts of air pollutants were transferred from the heavily industrialized and densely populated areas in central Europe to the surrounding regions (1), and through the UN Economic Commission for Europe (ECE) an attempt was being made to establish a common eastern and western European programme to examine the emission, dispersion and deposition of major pollutants, particularly the acidification of the precipitation.

Much of the initiative in this matter had been taken by the Nordic countries. As in the case of the OECD-project, it was decided to establish a Nordic expert group to take care of the planning and preparation of the programme, and to coordinate the programme within the Nordic countries. The expert group was established in 1975 with one representative from each country, but in practice representatives of all the participating laboratories have attended the meetings of the expert group when necessary.

The national members of the committee have been:

Denmark: H. Flyger, Danish Air Pollution Laboratory (DMI),
Risø.

Finland: A. Kulmala, Finnish Meteorological Institute (FMI),
Helsinki

Norway : B. Ottar (chairman) Norwegian Institute for Air
Research (NILU), Lillestrøm

Sweden : S. Laveskog, 1975-79, National Swedish Environment
Protection Board (SNV), Stockholm

R. Killingmo, 1979- " " " "

In addition, the Swedish Water and Air Pollution Research Laboratory (IVL) in Gothenburg has been permanently represented by C. Brosset, and the department of Meteorology, University of Stockholm (MISU), by L. Granat. Also representatives of the meteorological institutes in the Nordic countries have participated in many of the meetings.

During the period 1975-82 the programme has received 3 mill. NOK from the NMR. In addition, the participating institutes have contributed an equal amount in the form of man-hours, use of laboratory facilities, computer time, etc on a voluntary basis in order to make the programme succeed. An important force behind this has been the general scientific interest of the programme, which **directly and indirectly** has resulted in a number of scientific publications.

Based on the work of the expert group, detailed technical plans for EMEP were worked out during the period 1975-77, and in September 1977 EMEP was established under the auspices of ECE in Geneva with the support of UNEP and WMO (2). The technical administration of the programme was divided between a Chemical Co-ordinating Centre (CCC) at NILU in Norway and two meteorological synthesizing centres, one at the Norwegian Meteorological Institute (MSC-W) and one at the Hydrometeorological Institute in Moscow (MSC-E). The EMEP is revised by a Steering Body with one representative from each of the participating countries and became a part of the ECE Convention on long range transboundary air pollution in 1979.

Within the programme each country covers the costs of its own measuring stations. The central administration has been financed by UNEP and voluntary funds collected from participating countries. The Nordic countries have continued the work of the NMR expert group in order to provide necessary technical support for the programme.

The present measurements of EMEP include sulphur dioxide and sulphate on particles in the air and measurements of acidity, sulphate, nitrate and ammonium ions in precipitation at 70 stations in Europe. On a voluntary basis nitrate and ammonium ions in aerosols and nitrogen oxides are also measured at a few stations. A survey of position and programme of the EMEP-stations is given in Annex I (3).

For the second phase which started in 1981, it was strongly recommended to expand the minimum programme to include all relevant nitrogen compounds, but no agreement was reached on this point. Within the NMR programme methods for this expansion had already been developed, and as it became evident that years might pass before these methods could be used in EMEP, it was agreed to terminate the work of the expert group and to present a summary of the conclusions and their implications for future cooperative investigations of the regional air pollution in the Nordic countries.

2 RESULTS AND CONCLUSIONS FROM THE NMR-PROGRAMME

The NMR-programme included ten main tasks of research and development, all closely related to EMEP. The individual projects were carried out in different research institutes in the Nordic countries. In addition, some expert meetings on special topics, and a few seminars of more general interest, have been arranged. All reports from the programme are referred to in the text, but most of them are available only in one of the Nordic languages.

2.1 Measuring low concentrations of sulphur dioxide

The first task of the NMR programme in 1975 was to develop a more sensitive method for sampling and chemical analysis of sulphur dioxide. The standard Thorin method used in the OECD-project (4), had a sensitivity of about $5 \mu\text{g SO}_2/\text{m}^3$, while measurements of concentrations down to $0.1 \mu\text{g SO}_2/\text{m}^3$ were needed in background air.

Following an approach which had been successfully used for aircraft sampling (5), the 100 ml absorption solution used in the original method was substituted by a cellulose filter impregnated with a small amount of potassium hydroxide. This permitted the volume of the air sample to be increased from 4 to 20 m³/day, and the filter could be leached with 5 ml of water for the analysis. A main advantage of this approach is reduced contamination, due to the smaller volume and surface area of the glassware used in the chemical analysis, and a practical sensitivity of 0.1 µg SO₂/m³ was reached. Using ion chromatography with a pre-concentration column and specially cleaned filters, the sensitivity may be increased still further (6). Other advantages of the impregnated filter method are reduced problems with transportation of samples, and with two filters in series a single compact filterholder can be used to sample both sulphur dioxide and aerosol sulphate.

The method has been extensively tested in the laboratory (7,8,9,10) and under field conditions (11,12,13,14,15,16). The field tests were carried out for temperatures ranging from -21°C to + 7°C, and the sulphur dioxide concentration varied from 2 to 40 µg SO₂/m³. With four samplers of different construction, agreement within 10% was obtained; with samplers of the same construction, a mean deviation of 1.5% was obtained for 24 hour samples.

In order to obtain complete absorption of the sulphur dioxide, the impregnated filter should not be loaded to more than 40% of its theoretical capacity. With a linear velocity through the filter of 70 cm/sec, full absorption was obtained at relative humidities down to 20-30% RH, and with an addition of glycerol down to 2-3% RH. On the basis of these studies a final description of the method was worked out for EMEP (6).

At present, different methods are used in the EMEP-countries for the SO₂ determination. Intercalibrations show that it is difficult to obtain good comparability on this basis, although the methods may give excellent agreement when compared under ideal conditions. A first step to obtain more precise data, would therefore be to use one standardized method at all stations. For analyses of sul-

phur dioxide, impregnated filters combined with ion chromatography today seems to be the best alternative.

2.2 Measuring low concentrations of nitrogen compounds

The emissions of nitrogen oxides lead to the formation of nitrates, which may contribute 20-50% to the acidity of the precipitation in Scandinavia. Nitric acid is mainly formed from nitrogen dioxide by gas phase oxydation with OH radicals. The uptake of nitrate in aerosols depends on the chemical composition of the aerosol, relative humidity, temperature, and the partial pressures of HNO_3 (9) and NH_3 . Most of the nitrate in the precipitation is due to a direct uptake of gaseous nitric acid and NO_2 from the air.

These conditions also affect the sampling. When particles of different chemical composition are collected on a filter, they may give off or take up ammonia and nitric acid. The same applies to hydrochloric acid. The composition of the sample will then be different from the real composition of the aerosol in the atmosphere. At an early stage of the NMR programme it was therefore decided to develop methods which could provide true information about the chemical composition of the atmosphere, particularly the nitrogen components.

2.2.1 The nitrogen oxides

The concentration of nitrogen oxides in background areas is generally too low to permit the use of commercially available recording instruments, and with most manual methods the limited stability of the sample prevents long term sampling (17). The original Saltzman method (18) was developed for 1 hour samples, and the method of Jacob and Hochheiser (19), which for many years was used for 24 hour sampling in USA, has a low and highly variable collection efficiency ($\approx 30\%$). In 1975 a new method was recommended by the US Environmental Protection Agency, the TGS-ANSA method (20). This uses a mixed absorption solution with triethanol amine and guajacol, which act as an electron donor, converting NO_2 to nitrite ions. The spectrophotometric determina-

tion by diazotation is similar to the method of Griess-Saltzman, but a new coupling reagent, 2-anilino-1-naphthalene-sulfon-syre (ANSA), gives a more stable absorption complex. With an air flow of 0.2 l/min and 50 ml absorption solution, an absorption efficiency of 93% and a sensitivity of $5 \mu\text{g NO}_2/\text{m}^3$ was obtained.

Several attempts were made to improve the sensitivity of this method. However, increasing the air flow reduced the absorption efficiency (0.4 l/min - 90%, 2 l/min - 70%). Attempts were also made to use an impregnated filter in order to reduce the volume of the absorption solution. However, successful results reported by others (21), were not confirmed (22). Using two impregnated filters in series, an absorption efficiency of 65% for 0.4 l/min and 40% for 2 l/min was obtained. As a compromise, it was finally decided to use a sampling rate of 1 l/min with the TGS-ANSA method as described by EPA. This gives an absorption efficiency of 80% and a sensitivity of $1 \mu\text{g}/\text{m}^3$.

In 1980 a final field test with a series of 23 parallell measurements was made. Sampling periods of 1 to 4 days were used with two absorption tubes in series. The reproducibility was better than 2%, and 96% of the sample was absorbed on the first tube. The data showed no dependency on the sampling time. Other measurements showed that in addition to the recommended materials teflon, polypropylene and glass, also polyethylene could be used, and standard stock solutions would keep for a long time when stored cold in the dark.

During the last few years the instrumental methods have improved. Instruments with a sensitivity of about $5 \mu\text{g NO}_2/\text{m}^3$ are now available. This is sufficient for measurements in relatively clean areas, and a combination of instrumental and manual methods would therefore seem to be a useful approach. However, parallell measurements at the Rørvik station have shown that although the correlation between the methods is high (0.93), there is still considerable uncertainty with respect to the absolute values of the two methods for concentrations above $20 \mu\text{g NO}_2/\text{m}^3$.

2.2.2 Ammonia

Because of the rapid exchange between ammonia in the gas phase and ammonium ions in the aerosol phase, particles collected on a filter may, depending on the circumstances, pick up or give off gaseous ammonia. Also the pressure drop across the filter has an effect. In order to examine the real composition of the atmosphere, one may use denuder techniques. The air is passed through a 60-70 cm long glass tube of internal diameter 6-7 mm, the inside of which is impregnated with an absorbant. With laminar flow the particles will pass through the tube, while gaseous molecules are absorbed. In analytical chemistry such tubes were first used as scrubbers to remove gaseous components before the sampling of particles (23).

In 1979 IVL succeeded in using the tube as a sampler for ammonia, by impregnating the inner wall with an alcoholic solution of oxalic acid (24), and an intercalibration was arranged between 5 Nordic laboratories. Each laboratory prepared a number of tubes which were sent to the pilot station at Rørvik. Over a period of 10 days, two tubes from each laboratory were exposed for 24 hours with an air flow of 3 l/min. The samples and the blanks were sent back to the laboratories and analysed. Most of the measurements agreed well. However, all laboratories had some values which were far off. This also applied to the blanks. The conclusion was that the method could be used for routine analyses, but the contamination possibilities would have to be handled with extreme care (25).

2.2.3 Gaseous nitric acid

In this case different absorbants were first tested with a filter technique (26). The absorption of ammonia by filters impregnated with oxalic acid is a simple addition reaction, and the efficiency is 100% for air velocities up to 30 cm/s. By the absorption of HNO_3 on a NaCl impregnated filter, HCl has to be driven off. This reaction takes more time and the efficiency of the filter drops to 97% at 19 cm/s. The use of K_2CO_3 impregnated filters required

a certain level of moisture in the air, and the velocity through the filter was limited to 15 cm/s. Various amines were also tried as absorbants for HNO_3 , but satisfactory results were not obtained. Finally, Na_2CO_3 which had been successfully used to adsorb HF (27), gave the desired results. With this absorbant used in the denuder a detection limit of 0.04 ppb was obtained for 24 hour samples (28).

The denuder tube has also been used to examine reactions between the particles on the filter. Both the composition of the sample and the pressure drop across the filter are important in this case. The experiments further showed that some HNO_3 is absorbed to the surface of almost all materials (glass, metals, plastics). Possible losses in inlet tubes and filter holders should therefore always be considered.

2.2.4 Conclusions

The results show that it will be possible to measure the concentration of gaseous nitrogen components in the background air with sufficient sensitivity and without interference from the aerosol. If in addition, the two main aerosol fractions ($\gtrsim 2 \mu\text{m}$) are collected and analysed separately, it may also be possible to examine the chemical equilibrium composition of the atmosphere, as discussed in the next section.

Some more experience with the methods is required before they can be recommended for routine measurements in EMEP. In particular, there is a need to establish quantitative agreement between the TGS-ANSA method and the fluorescence instruments commonly used for the NO_x analysis.

2.3 Fractionated sampling of aerosols

After emission, the chemical composition and the size distribution of the aerosols change systematically with time. The very fine particles ($< 0.1 \mu\text{m}$) agglomerate rapidly and after some hours most of the pollution derived particles are found in the accumulation

mode between 0.1 μm and 2 μm . Also many of the gaseous components end as aerosols in this size fraction. The sedimentation velocity of these fine particles is negligible, they therefore represent the main component of the long range transport.

Larger particles ($>2 \mu\text{m}$) are usually formed by various mechanical processes. Normal components are wind blown dust and sea salt particles from the surroundings of the measuring point.

For a given source area, the particles in the accumulation range have a mixed composition determined by the emissions of that area. If the polluted air later passes another source area, the new particles agglomerate faster among themselves than with the older particles. After a while, one is therefore left with two sets of particles in the accumulation range, one for each of the source areas. Because of their larger size, further agglomeration and growth of these particles is negligible. The situation is complicated by the rapid exchange which takes place between gaseous components as NH_3 , HNO_3 and HCl , and the corresponding ions in the particles. The mean composition of particles collected on a filter may therefore differ from the actual composition of the free particles in the atmosphere. It was therefore agreed to test different techniques for separating the aerosols in two main fractions $\geq 2 \mu\text{m}$.

In March-April 1977 several types of impactors and cyclones, partly developed at IVL (29), MISU (30) and DML (31) were tested at the pilotstation Rørvik. In addition, the relative composition of small and large particles was examined by MISU at their test station at Velen, west of Stockholm (32). The sulphate measurements at Rørvik showed good agreement, with 80-90% of the sulphate on the fine particles. For sodium in the coarse fraction (sea salt), the agreement was also good. For other components (Ca^{2+} , NO_3^- , NH_4^+ , H^+ , and Cl^-) there was, however, little agreement between the different measurement techniques used.

The experiments were repeated in March 1978 (33). This time the chemical analyses were carried out with ion chromatography and particles deposited in the air intake were washed out and analysed

after each measurement. Also this time very satisfactory results were obtained for sulphate and sodium. The results further showed that significant amounts of the larger particles were deposited in the air intake. These particles reacted with some of the small sulphate particles which led to emissions of ammonia and a too high concentration of ammonium ions in the fine particles.

The last test was carried out in the winter 78/79 (34). This time four different types of instruments were tested:

- 1) Virtual impactor, separating the particles at $2 \mu\text{m}$
(18-19 m^3/d)
- 2) Samplers with impactors (25 m^3/d) or cyclones (100 m^3/d)
to remove the coarse particles, together with samplers with
no size separation (the difference method).
- 3) Samplers with double filters (50 m^3/d) with separation
point at $2.5 \mu\text{m}$ (the two-filter method).
- 4) Samplers with a single filter (50 and 15 m^3/d), and separation
of larger particles by sedimentation (low intake velocity).

The results showed that in strong winds large particles were deposited in the air inlet of all instruments. The amount depended on the shape of the air inlet and increased with low intake velocity. This particularly showed up in the measurements of the Cl^- ions, most of which were on the larger particles. The nitrate ions were distributed between the large and the small particles, and the result was very dependent on the separation point of the sampler. Most of the sulphate and ammonium ions were found on the small particles. When small and large particles were mixed on the filter, chemical reactions took place, also the pressure drop over the filter was of importance for the final composition of the sample.

A comparison of the different samplers favoured the double filter method. It gave the best agreement with the mean values for all the instruments tested, and the equipment is the simplest. This method has since been further tested at DML (35,36,37). These measurements show that there is a certain risk that coarse par-

ticles may roll off the coarse filter if this is not coated with a little high vacuum oil. Also a certain amount of fine particles may be collected by the deposited coarse particles when the sample becomes very dense.

If one is only interested in the fine fraction, a cyclone or an impactor may be used to remove the coarse particles. The difference method does, however, give far to inaccurate results for the coarse fraction. The virtual impactors are useful, but with the instruments tested, the results obtained for the coarse fraction were too variable. Regardless of which type of sampling instrument is used, there are systematic, but usually insignificant differences between the instruments. For a large network of sampling it would still be an advantage to use one standardized type of sampler.

2.4 The long range transport of micro-pollutants

The term micro-pollutant includes toxic organic compounds and trace elements which are present in the air in very small amounts, but may build up harmful concentrations in the environment by accumulation within the food chains. Well known examples are mercury, cadmium, DDT and PCB. Also the micro-pollutants are transported over long distances, and some may in a long term perspective be as important as the sulphur pollutants and the acidification of the precipitation. Measurements of trace elements and trace organic components may also be of use in identifying source regions and types of sources.

In order to obtain in a first survey, a symposium on the occurrence and possible effects of micro-pollutants in the Nordic countries was organized in 1978 (38). The meeting concluded that the micro-pollutants represent a possibility of future damage to the environment, but too little information was available for any definite conclusions.

2.4.1 Trace elements in aerosols

To determine the small amounts of trace elements in aerosols, high volume sampling techniques is normally used together with highly sensitive multi-element methods for chemical analysis like atomic absorption spectroscopy and neutron activation analysis. A method of particular interest is proton induced X-ray emission (PIXE). With this non-destructive method all elements heavier than aluminium can be determined in relatively small samples, which afterwards may be analysed for anions, etc. by other methods.

During the first half of 1980, 2 months of daily aerosol samples were collected at Virolahti in Finland, Rørvik in Sweden and Birkenes i Norway (39). The two-filter method was used, and both the fine and the coarse fractions were analysed, first by PIXE in Denmark and afterwards by wet chemical methods in the countries where the samples had been collected. Statistical analysis of the data showed clearly the dominans of pollution derived components in the fine particles, and the prevalence of soil and sea salt components in the coarse particles. Comparison of the time series of data also showed characteristic properties of the air pollution at the stations. At Rørvik and Virolahti, which are situated closer to the sources of air pollution in Central Europe, concentrations well above background values were measured all the time. At Birkenes very low concentrations of pollution derived components were observed on about half the days, when the wind was from northerly directions. Still, the data from the stations Birkenes and Rørvik were well correlated on a 24 hourly basis, while the station Virolahti clearly belonged to a different part of the European air shed.

The excellent agreement obtained in some cases and not in others, when the same element was analysed by PIXE and by other methods in the three countries, showed that there is still room for improvements with respect to the routine sampling and chemical analyses (40).

Multivariate statistical analysis of aerosol data from stations on Grenland (41,42) shows the presence of up to five main types of aerosols, derived from local soils, sea salt, and air pollution. A similar analysis of Norwegian data gave only the last two components, and the relative amounts depended on the distance from the coast line.

During the period June-November 1982 the two-filter method and PIXE analysis was used to examine the occurrence of air pollution at the Faeroe Islands (43). By the use of air trajectories and multi-variate statistical analysis of the fine and the coarse particle fractions, the composition and origin of the principal pollution components were identified.

These examples show that a combination of size fractionated aerosol sampling, more detailed chemical analyses and advanced statistical analysis of the data (including trajectory analysis) can provide much more precise information about the long range transport of air pollution than available today. Similar conclusions also apply to the local and mesoscale air pollution problems.

2.4.2 Elementary carbon

Elementary carbon undergoes no chemical reactions in the atmosphere, and is only removed by dry or wet deposition. It may therefore be used as an internal standard to estimate the chemical reactions of other pollutants in a series of samples. Studies have shown that simple reflection measurements according to the OECD-method (44), give a surprisingly good measure of the content of elementary carbon in filter samples collected in relatively clean areas. This has been checked with both the photoacoustic detector (45) and Raman spectroscopy (46). The latter methods give less scatter, but the correlation with the simple reflection measurements is very satisfactory.

However, for general use in background areas these methods are not sufficiently sensitive, and the absolute calibration of the methods represents a problem. At IVL a new ion chromatographic

method has been developed for determination of carbon dioxide after combustion of the soot particles collected on a glass fibre filter (47). At MISU a method has been developed in which the particles are collected on a microsorban filter (48). The filter is dissolved and the light absorption of the solution measured. This method has since been combined with PIXE analysis of the same filter. At DML a third method based on elastic proton scattering from the particles (PESA) has been developed for quantitative analysis of the elements C, N and O in filter samples with a detection limit of respectively 3,1 and 1 $\mu\text{g}/\text{m}^3$ air (49). The two-filter method was used for separate sampling of fine and coarse particles. When combined with PIXE analysis, $99 \pm 9\%$ of the total mass in the fine particle fraction was identified and $90 \pm 9\%$ in the coarse fraction. It is believed that the techniques now available, should permit measurements of elementary carbon at all background stations, but it remains to demonstrate the usefulness of such measurements in remote areas.

2.4.3 Organic components

The emission of reactive hydrocarbons of low molecular weight are of major interest in connection with the formation of photochemical oxidants, but only a few European countries have worked out any emission inventories for organic components. Concerning toxic trace components, the interest is centered on persistent and genetically active substances, such as PAH and polychlorinated hydrocarbons.

The use of polychlorinated hydrocarbons as pesticides has been severely restricted in most countries in the temperate zone, but in the tropical and subtropical areas enormous quantities are still used to fight malaria. The world production of DDT has not been much reduced, and probably the total consumption of polychlorinated hydrocarbons as pesticides amounts to more than 700.000 tons annually. The production of PCB (polychlorinated biphenyls) has been much reduced, but not stopped all together. Furthermore, a few hundred thousands tons of PCB used in large

transformers and as hydraulic fluids are being re-circulated. Also the plastic industry produces large amounts of chlorinated organic waste materials. Locally, the dumping of these materials has caused considerable problems, and today these waste products are preferably burned at high temperature.

All these substances have a low vapor pressure, also in the solid state. They are therefore slowly distributed all over the globe, and systematically transferred from warmer to colder regions. Their presence in remote areas was first demonstrated by analyses of samples which had been enriched within the natural food chains. Today methods are available for direct analysis of these compounds in air and precipitation. For air the PUR-sampler has been successfully used in the Arctic (50), and when the chemical analysis is made with gas chromatography/mass spectrometry using negative ions produced by chemical ionization extreme sensitivity may be obtained (51). This is, however, a relatively costly method. For routine measurements of aerosols collected on a filter, simple fluorescence measurements of an alcoholic extract have therefore been tested at IVL. The results show that this may be a useful approach for routine determinations in special cases (52).

Precipitation measurements are also useful to examine the occurrence of trace components. During the precipitation scavenging process most of the aerosol in the air is deposited with the precipitation. In this way substances which are absorbed to the aerosol particles may be deposited even if they are almost insoluble in water. In this connection different extraction methods for ppt-concentrations of chlorinated hydrocarbons have been examined at NILU (53). Further development of the XAD-2 extraction method has resulted in good recovery and reproducibility for polychlorinated benzenes and pesticides in the range 1-30 ppt in water and snow samples (54). The method is now used to analyse snow samples from the Arctic.

2.5 The measurements systems

Most of the chemical measurements used to verify calculated air pollution concentrations are collected at ground stations. For the long range transport of air pollutants measurements from aircraft represent indispensable additional information. But, only during the later years instruments have become commercially available which make continuous recording of air pollutant concentrations from aircraft practicable. Most of these instruments are, however, not sufficiently sensitive for background measurements. The selection of representative sites for background stations therefore still represents an important issue.

2.5.1 The Nordic background station network

At a meeting in Helsinki 1976 a coordination of the measurements at background stations in the Nordic countries was discussed. It was pointed out that background measurements usually serve three different purposes. Daily or more frequent measurements are used to verify trajectory or model calculations of the long range transport of air pollutants. Monthly measurements of precipitation and air pollution are commonly used to estimate the deposition of air pollutants in an area. Annual or seasonal mean values may be used to estimate regional or global trends.

A station network covering a larger geographical area, would improve the possibilities of examining the transfer of air pollutants to the Nordic countries from different source regions, and of studying the effects of different climatic conditions on the deposition and chemical transformation of the pollutants. Furthermore, testing and development of methods should be part of the integrated programme.

In order to specify a station network, the whole Nordic region was divided into areas of relatively uniform wind and temperature conditions. Within each of these areas it was decided to establish a minimum of one station (55). The resulting network of background stations is shown in Annex I. Apart from minor displacements in

order to improve the representativity of a station, this network has not been changed. Additional stations have, however, been established at the Faroe Island and in the Arctic. For the EMEP program daily samples of air and precipitation are collected at all these stations for subsequent chemical analysis. More comprehensive measurements are made at some of the stations, particularly at the Rørvik station in Sweden.

The data have primarily been used to verify atmospheric transport and deposition calculations. Long term sampling for simple trend analysis is problematic. The annual variations of the meteorological conditions may affect the observed annual mean concentration much more than changes of the emission pattern. Long time series are therefore required in order to obtain reliable trends. It was therefore recommended to examine the transfer of the pollutants from their source regions throughout the year, and use the data to correct for the annual meteorological variations. Trend indications could then be obtained from shorter periods of observation.

2.5.2 Precipitation measurements

Measurements of the chemical composition of precipitation constitute an important part of the monitoring of air pollutants. As sampling and chemical analysis is relatively simple in this case, a number of precipitation stations are in operation in the Nordic countries in addition to the regular EMEP stations. At these stations different methods are often used. In February 1981 these methods were discussed at a meeting arranged by MISU in Stockholm. The meeting gave a useful survey of the advantages and disadvantages of the different methods (56) used in the Nordic countries. A point of particular interest is the use of "wet only" samplers, i.e. samplers with a lid which opens only when it rains. The conclusion was that in forested background areas samplers without a lid may be used provided the collection vessel is changed or cleaned each day. For monthly samples a lid is recommended. If not available, at least a screen should be used in the funnel to hold back contaminating

materials. The choice also depends somewhat on which components are to be analysed.

2.5.3 The representativity of ground stations

In the EMEP a grid of 150 km and 6 hourly trajectories are used to describe the atmospheric transport. The calculated data thus represent mean values in time and space, and they are normally compared to 24 h mean values measured at ground level. In the OECD-project, an attempt was made to use 6 hourly mean concentrations. This did not, however, improve the situation, because the daily variations of the vertical wind and stability could not be included in the one-layer atmospheric dispersion models used.

In order to examine the local representativity of such data, 6 identical instruments for measuring sulphur dioxide and sulphate particles were mounted in a test field in Finland during the winter 1978/79 (57). Two stations were placed closely together in the middle of an open field. The other four stations were placed in different positions up to 400 m from the first pair. For 6 hourly mean values the correlation varied from 0.99 for the two neighbouring stations to 0.93 for stations further apart.

The mean deviation between the two neighbouring stations was 11% for a mean value of $29 \mu\text{g}/\text{m}^3$. The mean deviation for all stations was slightly higher, and analysis showed that these differences were more related to the position of the station relative to minor emission sources in the area, than to the local terrain formation. For 24 h mean values the difference between neighbouring stations was reduced from 11 to 5%.

For measurements at one station the standard deviation was $22 \mu\text{g}/\text{m}^3$, which shows that variations in the weather conditions have a much larger influence on the result than the location of the station. Under stable conditions with weak winds, the effect of small local emission sources increased from 11% to 22%. On the other hand, contributions from outside were always first noted at the most freely exposed station.

Similar studies in different types of terrain and on the scale used in the long range transport models would undoubtedly be of value in selecting station positions.

On a larger scale, nephelometer measurements carried out by MISU in the surroundings of the station Velen in central Sweden showed that the overall light scattering from particles in the atmosphere at a well exposed measuring station was representative for areas of several thousand km², i.e. comparable to the grid squares in the numerical simulation models.

The representativity of precipitation measurement stations has been extensively investigated at MISU. The results show that the local surroundings of the stations are very important, mainly by influencing the local wind field, and guidelines for the siting of precipitation stations have been worked out (58)..

2.5.4 Aircraft measurements

In the OECD-project measurements from aircraft helped very much to clarify the air pollution transport in the atmosphere.

Extensive measurement programs were carried out, particularly by MISU and NILU (59),, and instruments and measuring methods were developed within the NORDFORSK programme (60). Since 1975 all the Nordic countries have access to aircraft which can be used for air pollution measurements.

When the NMR-programme started in 1975, it was believed that aircraft measurements would be extensively used also in EMEP, and in the autumn of 1975 an intercalibration of the instruments used to measure sulphur dioxide and sulphate particles was carried out (61). The sampling was based on the use of an aerosol filter, followed by an impregnated filter for sulphur dioxide. In a parallel test of the instruments at DML 50 samples of air were collected. The sample size varied from 0.5-2 m³ of air. The concentration of sulphur dioxide was most of the time below 15 µg/m³, and the concentration of particle sulphate was below 10 µg/m³. All

filters were first analysed by XRF at the Institute for Energy Technology in Norway, and then by wet chemical methods in each country. In spite of the relatively low concentrations, good agreement was obtained.

In July 1976 a series of parallel measurements were made between the Danish and the Norwegian aircrafts (62). For aerosol sulphate good agreement was obtained, while for sulphur dioxide considerable differences were observed occasionally, probably because of the low concentrations measured ($<5 \mu\text{g SO}_2/\text{m}^3$).

The available methods were considered satisfactory, and in March 1977 an evaluation was made of the possible uses of aircraft measurements. It was concluded that:

- Coordinated measurements during air pollution episodes were considered highly desirable, but the difficulties in organizing sampling of the same air mass at consecutive times would have to be looked into.
- An attempt should be made to examine the representativity of ground stations by measuring the vertical profiles of sulphur dioxide and particle sulphate.
- The possibilities of quantitative sampling of cloud droplets for a given air volume should be looked into.

By this time it had, however, become evident that funds would not be available for any coordinated aircraft measurements in EMEP. The programme was therefore concluded with measurements of a few vertical concentration profiles. In June 1978 NILU made some measurements in the outer Oslofjord (63) in a situation with transport of air pollutants from United Kingdom to Norway. The data were used to calculate the transformation rate of sulphur dioxide to particle sulphate. The result agreed well with estimates made in connection with the OECD-project. In southern Finland the FMI measured a number of profiles in connection with a regional model calculation.

A main problem in connection with aircraft measurements has been the lack of techniques which makes it possible to utilize the high speed of the aircraft. Measurements of background concentrations of sulphur dioxide and particle sulphate require a sampling time 20-30 min. During the later years this situations has changed. New instruments permit detailed characterization of the size distribution of the aerosol from the aircraft, and chemical instruments are now available which are sufficiently sensitive to make continuous recordings of the concentration of many pollutants in background areas from aircraft.

2.5.5 Co-ordinated publication of nordic environmental data

In 1976 the Nordic ministerial Council had suggested the establishment of an environmental data bank, and it was discussed to coordinate the publication of air pollution data from all stations in the Nordic countries. A survey showed that normally daily, weekly or monthly samples were collected and that it took about two months before all samples were analysed. It was suggested to limit the reporting to daily and monthly mean values for stations which had been in operation for one year or more. Data collected for other intervals would be re-calculated and reported as monthly means when possible. It was further recommended to evaluate and distribute the data to the Nordic laboratories as an addition to EMEP-data. It would be few if any data from the nordic stations which could not be included in this plan. The costs would be relatively small, and the data would be available in a compiled and organized form at agreed times for all laboratories.

However, gradually it became evident that no one was willing to pay for publication of the air pollution data, and the expert committee came to the conclusion that it would be no point in starting the work if the data could not be compiled and examined over a period of at least five years. On this background the effort was limited to the publication of a survey with information about the positions of the Nordic stations and their measuring programmes (64).

2.6 Long range transport modelling

A main task of EMEP is to provide a quantitative description of emission, dispersion and deposition of sulphur pollutants in Europe. When the programme started, it was logical to use the model developed within the OECD-project for the same purpose, and try to develop this further, primarily by specifying in more detail the empirical parameters used in the model. There is also a need to examine the long range dispersion of nitrogen oxides and the formation of photochemical oxidants. A first requirement in this connection is to establish the necessary emission surveys.

2.6.1 The emission surveys

The first survey of the sulphur dioxide emissions in Europe was worked out for the OECD-project (65). For many of the EMEP countries this survey has since been updated (66). For western Europe the national emissions may be accurate to 10-15% and the uncertainty of a single grid element within $\pm 50\%$. For eastern Europe the national emission figures are more uncertain, and as little information has been received concerning their geographical distribution, these national emissions have been distributed in a grid system on the basis of population density and available information on the geographical location of major industries.

On this background the question was raised in 1977 if the emission fields could be estimated from trajectory calculations and daily measurements at the EMEP stations. A trajectory calculation method was worked out and tested on some of the OECD-data (67,68). Three examples were calculated, each with about 1000 station days. The results showed that such calculations can be used to estimate the emissions from grid elements not too far away from the measuring station, and some of the calculated values agreed well with the emission survey. For practical use a much larger data set would have to be used, for instance 10.000 station days, and it will be necessary to use statistical methods to evaluate the data. So far it has not been possible to continue work in this direction.

In 1979 a more detailed comparison of sulphur dioxide emissions and population density was made for the grid used in EMEP (150 km x 150 km). Available population statistics were collected for all European countries, and a complete population density map was worked out (69). For Western Germany where a detailed emission survey was available, it turned out that within $\pm 25\%$ the emissions for these grid elements were proportional to the population density. The same was found for the United Kingdom. The necessary data were also available for France, but in this case the scatter was much larger and the grid length had to be doubled in order to obtain a nationally representative sample of sources types in each grid element.

This result rests on the statistical distribution of the emissions in larger areas, and deviations do occur. Thus, the sulphur dioxide emission in London is less than the calculated value because the industrial activity is relatively small compared to the population density, while the Birmingham emission is somewhat higher than the national mean. Exercising some care, this result has been used to re-evaluate the sulphur dioxide emissions in some of the countries.

The present emission survey may still contain considerable errors. Data for single grid elements in eastern Europe may be more than a factor 2 wrong. This particularly applies to the USSR, from where no data for the geographical distribution of the emissions have been obtained.

The emissions of nitrogen oxides have been evaluated in a similar way (70). Data from Western Germany, United Kingdom and France showed that there is close proportionality between the emissions of sulphur dioxide and nitrogen oxides. As about 50% of the nitrogen oxide emissions originate from motorized traffic, this means that where industry and people are located, one will also find the car traffic. The proportionality factor must be given by the ratio between the total national emissions of sulphur dioxide and nitrogen oxides, which can be estimated from national

production and consumption figures with the use of the emission factors. On this basis an emission survey for nitrogen oxides in Europe has been worked out. It may be noted that although the emission value for a single grid element may be highly uncertain, the position of the major source areas will be correct. Some applications indicate that the survey is sufficiently accurate for long range transport calculations of photochemical oxydants (71).

2.6.2 Atmospheric transport modelling

In March 1980 a meeting of experts from the nordic countries was held at NILU in order to survey the possibilities of improving the long range transport calculations of air pollutants (72). It was concluded that a significant improvement of the models now used would require a revision of several model parameters which today are given in a very approximate manner. Specifically, the meeting recommended that a detailed investigation of the precipitation scavenging process was undertaken. Preliminary plans for a study of orographic precipitation on the south coast of Norway have since been workd out (73, 74). This study is still under serious consideration, but funds have not yet been available.

In the follow up of the recommendations from the meeting only a few studies have been undertaken within the NMR-programme. At DMI the variation of different meteorological parameters with wind direction have been examined (sector analysis) (75). Upper air data for 5 years have been analysed for 4 stations (København, Stavanger, Slesvig, Visby) and mean values calculated for mixing height, relative humidity, and atmospheric stability.

A study of statistical methods to handle variations in time and space of precipitation data has been made at MISU (76).

At FMI a study of the mixing height and its variation with the seasons was carried out (77). In 1982 FMI also carried out a study of the precipitation process based on radar observations and chemical analysis of the air and the precipitation (78) to see if one could distinguish between different types of precipitation on the basis of chemical composition. The measurements were carried out in the Helsingfors area. However, the radar observations did not give the necessary details about the different types of precipitation.

In addition to the NMR programme, MSC-W has continued their studies of the model parameters (79). These studies have all contributed to a better understanding of the significance of the simplifications which one always has to make in atmospheric dispersion models. Much work remains to be done, however, before all relevant factors have been examined.

3 FUTURE ASPECTS

The OECD-project showed that the main cause for the acidification of the precipitation in Europe is the emission of sulphur and nitrogen oxides from the use of fossile fuels for heat and energy production, motorized traffic and special industries. In the EMEP programme, where also the eastern European countries participate, the work has been focused on the emission, dispersion and deposition of the sulphur components, as these were considered to be the most important in connection with the acidification of the precipitation. Also, useful methods for sampling and chemical analysis were available for the sulphur components, while measurements of nitrogen oxides and other nitrogen components in background areas involved considerable problems.

Within the NMR programme, the ground has been laid for an expansion of the EMEP to include the nitrogen compounds and a more detailed study of the composition of the polluted atmosphere. On the theoretical side, statistical methods have been used to analyse the observed data and to examine the parameters of the atmospheric

dispersion models. A first European emission survey for nitrogen oxides has been prepared. The results of the NMR programme show that much can be done to improve the quality of the work within EMEP, both with respect to sampling and chemical analysis and to data evaluation. Within EMEP one has not, however, been able to make use of these possibilities. At the same time other studies show that the regional air pollution in Europe includes an increasing number of chemicals, and affects larger and larger areas.

There is evidence that the effects of the acid precipitation observed in rivers and lakes in Scandinavia, and the damage to the forests on the European continent are the results of a long term accumulation of sulphate in the soil, which has led to the release of harmful concentrations of toxic aluminium hydroxy ions in the ground water. In some areas this aluminium now has to be removed from the drinking water. An important consequence of this view is that it may be more difficult to reverse the present development than previously anticipated.

The emissions of sulphur dioxide have levelled out during the later years. However, the emissions of nitrogen oxides have not, and the increasing content of nitrate in precipitation has recently been related to the extensive fish kills observed in the North Sea due to an overproduction of toxic algae. In Scandinavia the nitrate deposited is rapidly consumed by the vegetation, which benefits from this. There is, however, a limit to how much can be disposed of in this way, and in other areas also the nitrates add to the changes of the soil composition.

Other measurements show that the concentration of ozon in Scandinavia periodically exceeds values which in North America have led to vegetation damage and extensive insect attacks. Similar cases in Europe have not been examined in detail. The photochemical oxidants also increase the general oxidation potential of the atmosphere. Thus the oxidation rate of sulphur dioxide is much higher in summer than in winter. Recently it has been shown that the photochemical radicals also increase the oxidation rate of

naturally occurring mercury vapours, and that this explains the disturbingly high mercury levels found in predatory fish from many remote areas.

These examples show that the regional air pollution problem in Europe includes much more than the emission of sulphur dioxide and the low pH of the precipitation. The basic problem is that the emissions of air pollutants in the industrialized and densely populated regions exceed the amounts which can be rendered harmless by dispersion into the atmosphere. The use of tall chimneys and the spreading of industry and traffic, means that the local concentration level is reduced by transferring the pollutants from a local to a regional air shed, in much the same way as when a sewer is led directly to the sea and not into the local lake.

However, the capacity of the regional recipient is also limited. Most of the pollutants stay within the lower 2-3 km of the atmosphere, and beyond a distance of 100-200 km from a source area there is no further dilution of the pollutants except by dry and wet deposition.

During this transport, chemical reactions change the properties of the pollutants. The acute poisoning of the vegetation by sulphur and nitrogen oxides is changed into the chronic effects of sulphate deposition in soils and nitrate fertilization of the sea. The noxious effects of the oxidants change into a long term weakening of the vegetation, followed by insect attacks. Volatile toxic pollutants slowly accumulate in the colder regions, others affect the radiation balance and may cause a change of climate. These apprehensions may or may not represent serious threats. The problem is that if we wait to see, then it may be too late to do anything about it when the effects are observed. The only way in which mankind may remain in control, is to examine these and other possibilities through international programmes like EMEP, starting with regional surveys as a basis for the global studies.

On this background the expert group has recommended a Nordic pilot programme to examine the long range transport of air pollutants in North Western Europe in greater detail. In this programme the methods described, will be used to examine the chemical composition of the atmosphere and the physical and chemical reactions taking place during the transport of the pollutants. It will primarily be a pathfinding programme to look into possible long term problems, which later may be followed up by routine monitoring in EMEP or other programmes. The pilot programme will also provide the Nordic countries with more precise information about the air pollution than presently available. Co-operation will be sought with interested research institutes in other countries.

4 REFERENCES

- (1) OECD (1979) The OECD programme on long range transport of air pollutants. Measurements and findings. OECD, Paris.
- (2) Ottar, B. (1977) International agreement needed to reduce long range transport of air pollutants in Europe. *AMBIO* 6, 262-269.
- (3) EMEP Expert Meeting on Chemical Matters (1982). Norwegian Institute for Air Research, Lillestrøm, Norway (EMEP/CCC-Report 1/82.)
- (4) Persson, G.A. (1966) Automatic colorimetric determination of low concentrations of sulphate for measuring sulphur dioxide in ambient air. *Int.J.Air Water Pollution* 10, 845-852.
- (5) Johnson, D.A. and Atkins, D.H.F. (1975) An airborne system for the sampling and analysis of sulphur dioxide and atmospheric aerosols. *Atmos. Environ.* 9, 825-829.
- (6) European Monitoring and Evaluation Programme (1980). Manual for sampling and chemical analysis: (EMEP/CHEM-3/77, with supplements.) Norwegian Institute for Air Research, Lillestrøm, Norway.
- (7) Lewin, E. (1975) Prøvetagning af SO₂ med impregneret filter. Bestemmelse af ammonium og nitrationer samt fri syre. Statusrapport pr. 31. desember 1975, Miljøstyrelsens Luftforureningslaboratorium, Risø, Denmark.
- (8) Lewin, E. and Zachau-Christiansen, B.
 - Supplerende interkalibreringsanalyser af flybårent utstyr. Svoveldioksyd og impregneret filter. Foreløbig rapport.
 - Svoveldioksyd og impregneret filter ved lave temperaturer. Miljøstyrelsens Luftforureningslaboratorium, Risø Denmark.
 - (1977) Efficiency of 0.5 N KOH impregnated filters for SO₂ collection. *Atmos. Environ.* 11, 861-862.
- (9) Zachau-Christiansen, B. (1979). Sammenfatning af tidligere undersøgelser over absorption af SO₂ på KOH-imprægnerede filtre. Miljøstyrelsens Luftforureningslaboratorium, Risø, Denmark (MST LUFT-B20).
- (10) Larssen, S. and Hanssen, J.E. (1980) Investigation of the KOH impregnated filter method for SO₂ sampling. Norsk institutt for luftforskning, Lillestrøm, Norway. (NILU TN 7/79.)

- (11) Lätttilä, H., Rautanen, Y. and Ruoho, T. (1977) Interkalibrering av provtagare för låga SO₂-konsentrasjoner. Meteorologiska Institutet, Helsingfors, Finland. Preliminär rapport, oktober 1977.
- (12) Lewin, E. (1979) Test of the FMI's calibration system for sulphur monitors by means of the permeation tube system used by DML. Miljøstyrelsens Luftforureningslaboratorium Risø, Denmark (MST LUFT-523.)
- (13) Ruoho, T., Lätttilä, H. and Rautanen, Y. (1979) Interkalibrering av SO₂-provtagare för bakgrundsstationer. Meteorologiska Institutet, Helsingfors, Finland.
- (14) Zachau-Christiansen, B. and Lewin, E. (1979) Opsamling av SO₂ på KOH imprægnerede filtre. Feltundersøgelse i København i vinteren 1978/79. Miljøstyrelsens Luftforureningslaboratorium, Risø, Denmark (MST LUFT-B21).
- (15) Zachau-Christiansen, B. (1980) Feltundersøgelse i et byområde og et baggrundsområde i sommeren 1979. Miljøstyrelsens Luftforureningslaboratorium, Risø, Denmark.
- (16) Hanssen, J.E. (1980) Sammenlikning av prøvetakere for lave SO₂ konsentrasjoner i luft. Norsk institutt for luftforskning, Lillestrøm, Norway.
- (17) Hanssen, J.E. (1977) Metoder for manuell bestemmelse av nitrogendioksyd (NO₂), en litteraturoversikt. Norsk institutt for luftforskning, Lillestrøm Norway. (NILU TN 11/77.)
- (18) Saltzman, B.E. (1954) Colorimetric micro determination of nitrogen dioxide in the atmosphere. *Anal. Chem.* 26, 1949-1955.
- (19) Jacobs, M.B. and Hochheiser, S. (1958) Continuous sampling and ultramicrodetermination of nitrogen dioxide in the air. *Anal. Chem.* 30, 426-428.
- (20) Fuerst, R.G. and Margeson, J.H. (1974) An Evaluation of the TGS-ANSA procedure for the determination of nitrogen dioxide in ambient air. EPA, Research Triangle Park, N.C., USA. (EPA-650/4-74-047).
- (21) Alary, J. Bourbon, P., Charn, P., Delaunay, C., Esclassan, J. and Lepert, J.-C. (1974) Sur une nouvelle methode de dosage de dioxyde d'azote present dans les atmospheres polluees, derivee de la methode de Griess-Saltzman. *J. Water, Air and Soil Poll.* 3, 555-562.
- (22) Ladegård, H. (1980) Utprøving av TGS/ANSA-metoden for NO₂ ved NILU. Norsk institutt for luftforskning, Lillestrøm, Norway (NILU TN 2/80.)

- (23) Coburn, W.G., Husar, R.B. and Husar, J.D. (1978) Continuous measurement and speciation of sulfur - containing aerosols by flame photometry. *Atmos. Environ.* 12, 89-98.
- (24) Ferm, M. (1979) Method for determination of atmospheric ammonia. *Atmos. Environ.* 13, 1385-1393.
- (25) Hanssen, J.E. (1980) Sammenligningsmålinger av ammoniakk i luft. Norsk institutt for luftforskning, Lillestrøm, Norway.
- (26) Ferm, M. (1980) Metod för bestämning av salpetersyra. Preliminary report. Institutet för Vatten- och Luftvårdsforskning, Göteborg, Sweden.
- (27) Pack, M.R. et al. (1959) Determination of gaseous and particulate inorganic fluorides in the atmosphere. *Soc. Testing Mat. Spec. Tech. Publ.* 281, 7-44.
- (28) Ferm, M. (1982) Metod för bestämning av gasformig salpetersyra och partikulär nitrat i atmosfären. Institutet för Vatten- och Luftvårdsforskning, Göteborg, Sweden. (IVL B-665.)
- (29) Johanson, B. and Steen, B. (1977) Framtagning av en enkel virtuell impaktor för flödet 20 m³/dygn och för provtagning av stoff i två fraktioner. Institutet för Vatten- och Luftvårdsforskning, Göteborg, Sweden. (IVL B-370.)
- (30) Granat, L. (1979) Utvärdering av utrustning för fraktionerad provtagning på atmosfärisk aerosol. Meteorologiska Institutionen, Stockholms Universitet, Stockholm, Sweden.
- (31) Heidam, N.Z. (1977) Beskrivelse af udstyr til fraktionert prøvetagning af aerosoler. Miljøstyrelsens Luftforureningslaboratorium, Risø, Danmark.
- (32) Granat, L. (1978) Aerosolforsök vid MISU som utförts med bidrag från Nordiska Ministerrådet. Meteorologiska Institutionen, Stockholms Universitet, Stockholm, Sweden (AC78-63).
- (33) Brosset, C. (1978) Provtagning av aerosoler jämförande försök med några provtagare utförda vid Rörvik nov-dec 1978 och jan-feb 1979. Institutet för Vatten- och Luftvårdsforskning, Göteborg, Sweden.
- (35) Heidam, N.Z. (1981) Review: Aerosol fractionation by sequential filtration with Nucleopore filters. *Atmos. Environ.* 15, 891-904.

- (36) Palmgren Jensen, F. and Kemp, K. (1979) To-filtermetoden og differensmetoden til størrelsesfraksjoneret prøvetagning. En feltundersøkelse i København. Miljøstyrelsens Luftforureningslaboratorium, Risø, Denmark (MST LUFT A14).
- (37) Kemp, K. (1981) Feltundersøkelse av "to-filter-sampler". Miljøstyrelsens Luftforureningslaboratorium, Risø, Denmark.
- (38) Laveskog, A. and Torsmark, U. (1979) Långväga transport av mikroforureningar. NMR-seminar oktober 1978 på Skytteholm. Statens Naturvårdsverk, Solna, Sweden (SNV PM 1131.)
- (39) Kemp, K. (1981) Analyse av mikrokomponenter på partikkel-fraktioner. (PIXE analyser). Miljøstyrelsens Luftforureningslaboratorium, Risø, Denmark. Foreløpig notat, jan. 1981.
- (40) Kemp, K. (1981) Sammenligning af analyseresultater fra to-filter sampler prøver. Miljøstyrelsens Luftforureningslaboratorium, Risø, Danmark.
- (41) Heimdam, N.Z. (1981) On the origin of the Arctic aerosol: A statistical approach. *Atmos. Environ.* 15, 1421-1427.
- (42) Heidam, N.Z. (1983) Observationer af den troposfæriske aerosol i Grønland. En sammenfatning for perioden 1979-1980. Miljøstyrelsens Luftforureningslaboratorium, Risø, Denmark (MST LUFT A-69).
- (43) Lewin, E. and Heidam, N.Z. (1983) Den Færøiske aerosols oprindelse. Miljøstyrelsens Luftforureningslaboratorium, Risø, Denmark (MST LUFT-B9).
- (44) OECD (1964) Methods for measuring air pollution. Paris.
- (45) Rosen, H., Hansen, A.D.A., Dod, R.L., Novakov, T. (1980) Soot in urban atmospheres: Determination by an optical absorption technique. *Science* 208, 741.
- (46) Rosen, H. and Novakov, T. (1977) Raman scattering and the characterization of atmospheric aerosol particles. *Nature* 226, 708.
- (47) Ferm, M. and Galle, B. (1982) Metod för bestämning av grafit i aerosoler. Institutet för Vatten- och Luftvårdsforskning, Göteborg, Sweden (IVL B666).
- (48) Heintzenberg, J. (1982) Measurement of light absorption and elemental carbon in atmospheric aerosol samples from remote locations. In: *Wolff, G.T. & Klimisch, R.L. (eds). Particulate carbon-Atmospheric cycle.* Plenum Press N.Y.

- (49) Kemp, K. (1983) Bestemmelse av elementært C,N og O i aerosoler med PESA. Miljøstyrelsens Luftforureningslaboratorium, Risø, Denmark.
- (50) Oehme, M. and Stray, H. (1982) Quantitative determination at ultra traces of chlorinated compounds in high-volume air samples from the Arctic using polyurethane foam as collection medium. *Fresenius Z. Anal. Chem.* 311, 665-673.
- (51) Oehme, M. (1983) Negative ion chemical ionization/high resolution gas chromatography - a powerful tool for air borne trace analysis. *Internat. J. Mass. Spectr. and in phys.* 48, 287-290.
- (52) Galle, B. (1982) Metod för bestämning av grafitinnhalt i partikler via deres fluorescens. Institutet för Vatten- och Luftvårdsforskning, Göteborg, Sweden (12.mars 1983.)
- (53) Oehme, M. and Manø, S. (1981) Sammenligning av ekstraksjonsmetoder for ppt-konsentrasjoner av klorerte organiske forbindelser i vann og nedbør. Statusrapport og foreløpige resultater. Norsk institutt for luftforskning, Lillestrøm, Norway.
- (54) Manø, S. (1982) Utprøving av forskjellige oppkonsentreringsmetoder for ppt-konsentrasjoner av polyklorerte hydrokarboner i vann. Norsk institutt for luftforskning, Lillestrøm, Norway.
- (55) Ottar, B. (1977) Koordinert måleprogram for luftforurensninger i Norden. Anbefalinger fra Nordisk Ministerråds ekspertgruppe for luftforurensninger. Norsk institutt for luftforskning, Lillestrøm, Norway (NILU TN 10/77.)
- (56) Granat, L. (1983) Redovisning från det nederbörds-kemiska arbetsmötet på Lejon-dals slott den 16.-18. feb. 1981. Meteorologiska Institutionen, Stockholms Universitet, Sverige.
- (57) Bremer, P. (1980) Jämförande SO₂-mätningar vid en bakgrundsstation. Meteorologiska Institutet, Helsingfors, Finland.
- (58) Granat, L. (1977) Siting Criteria for precipitation chemistry measurements. A Method for direct evaluations. The Meteorological Institute, Stockholm University, Sweden (AC-39.)
- (59) Semb, A. (1978) Aircraft sampling. Methods for the determination of sulphur dioxide and sulphate aerosol using a light aircraft. NORDFORSK, Miljøvårdssekretariatet, Helsingfors, Finland.

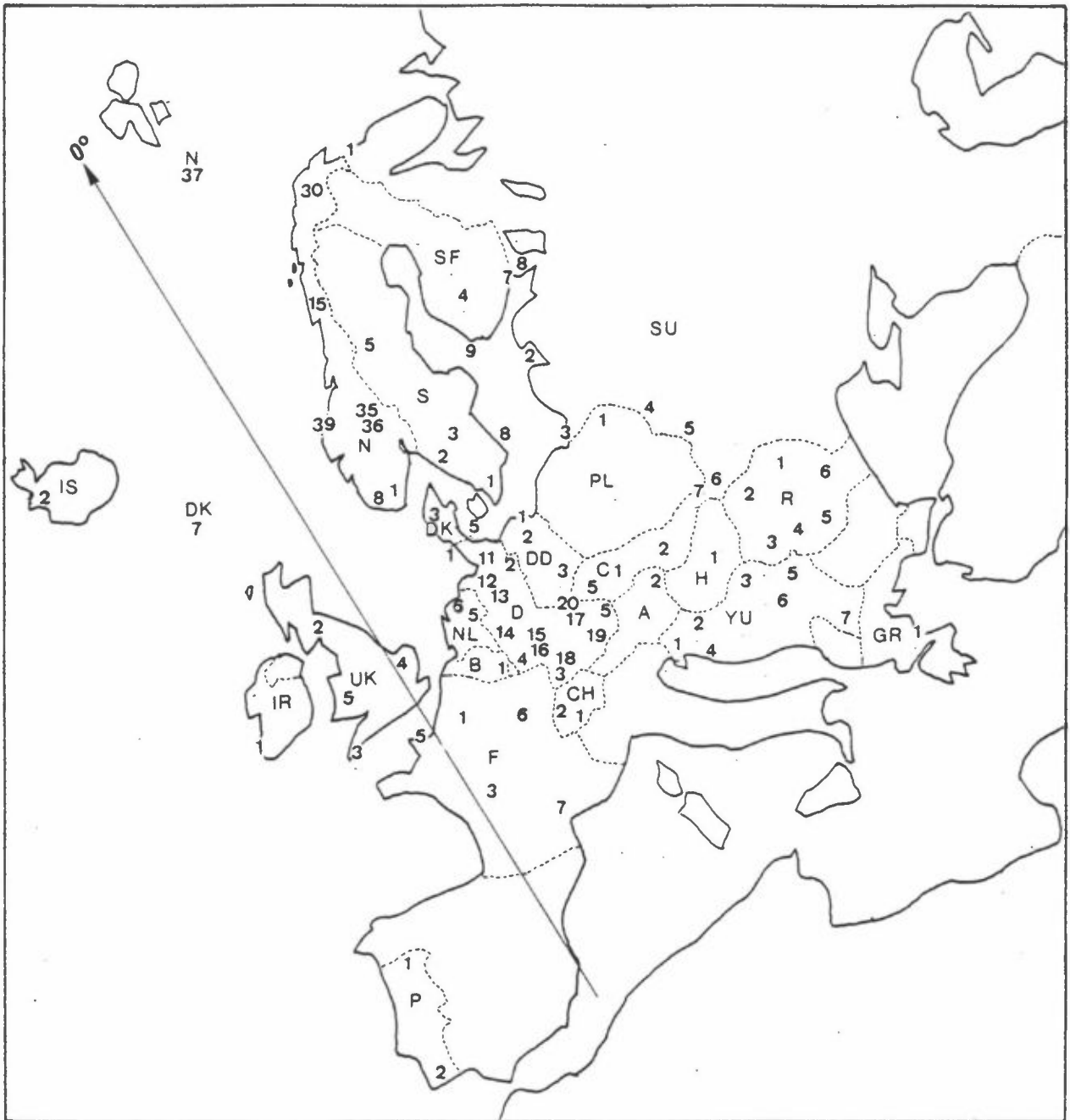
- (60) Ottar, B. (1976) Årsakene til nedbørens forsurening. NORDFORSK, Miljøvårdssekretariatet, Helsingfors, Finland. (Publikation 1975:10).
- (61) Heidam, N.Z. and Palmgren Jensen, F. (1977) Nordic inter-calibration of airborne equipment for measurement of sulphate and sulphur dioxide. Risø National Laboratory, Risø, Denmark (RISØ M-1941).
- (62) Gotaas, Y. (1977) Samflyging over Danmark 13. og 14. juli 1976. En sammenlikning av prøvetakerutstyr for svoveldioksyd og sulfat. Norsk institutt for luftforskning, Lillestrøm, Norway. (NILU TN 8/77.)
- (63) Gotaas, Y. (1982) Vertical distribution of sulphur in the atmosphere in a case of long range transport and the rate of transformation to sulphate. *Atmos. Environ.* 16, 1043-1046.
- (64) Miljøkvalitetsövervakning i Norden. Nordiska Ministerrådets sekretariat, Oslo, Norway. (March 1981)
- (65) Semb, A. (1982) The OECD study of long range transport of air pollutants. Source inventory. *Atmos. Environ.* 12, 455-460.
- (66) Dovland, H. and Saltbones, J. (1979) Emissions of sulphur dioxide in Europe in 1978. Norwegian Institute for Air Research, Lillestrøm, Norway. (EMEP/CCC-Report 2/79.)
- (67) Prahm, L.P., Conradsen, K., Eliassen, A. and Nielsen, L.B. (1979) Regional kilde identifikasjon. Miljøstyrelsens Luftforureningslaboratorium, Risø, Denmark (MST-LUFT-A13.)
- (68) Prahm, L.P., Conradsen, K. and Nielsen, L.B. (1980) Regional source quantification model for sulphur oxides in Europe. *Atmos. Environ.* 14, 1027-1054.
- (69) Amble, E. (1981). Estimation of the spatial distribution of the population and SO₂ emission in Europe and Turkey within the EMEP grid. Norwegian Institute for Air Research, Lillestrøm, Norway (NILU TR 8/81).
- (70) Semb, A. and Amble, E. (1981) Emission of nitrogen oxides from fossil fuel combustion in Europe. Norwegian Institute for Air Research, Lillestrøm, Norway (NILU TN 13/81).
- (71) Eliassen, A., Hov, Ø., Isaksen, I.S.A., Saltbones, J. and Stordal, F. (1982) A Lagrangian long range transport model with atmospheric boundary layer chemistry. *J. Appl. Meteorology* 21, 1645-1661.

- (72) Dovland, H. (1980) NMR-prosjektet "Overvåkingssystem for luftforurensninger" Teknisk møte om langtransportmodeller. NILU 4-5 mars 1980. Norsk institutt for luftforskning, Lillestrøm, Norway.
- (73) Whelpdale, D. (1981) Sulfate scavenging ratios at Norwegian EMEP-stations. Norwegian Institute for Air Research, Lillestrøm, Norway. (EMEP/CCC Report nr. 5/81.)
- (74) Whelpdale, D. (1981) Notes on a precipitation scavenging field investigation. Norwegian Institute for Air Research, Lillestrøm, Norway.
- (75) Buch, H. (1981) Sektoranalyse af relevante meteorologiske parametre for langtransport af luftforureninger. En statusrapport. Luftforureningsgruppen, Meteorologisk Institut, København, Denmark.
- (76) Hamrud, M. (1982) The effect of spatial smoothing on Lagrangian rainfall statistics. Meteorological Institute, Stockholm University, Stockholm, Sweden (CM-55).
- (77) Nordlund, G. (1981) Sektor- och årstidsvariation av spredningsparameteren blandingshøjd i Finland. Finlands Meteorologiska Institut, Helsingfors, Finland.
- (78) Bremer, P. Undersøkelser av nedbørutfellingsprosessen ved hjelp av radar og kjemiske analyser. Finlands Meteorologiska Institut, Helsingfors, Finland. Preliminær rapport, mars 1983.
- (79) Eliassen, A. og Saltbones, J. (1982) Modelling of long range transport of sulphur over Europe: A two-year model run and some model experiments. Norwegian Meteorological Institute, Oslo, Norway. (EMEP/MSC-W Report 1/82.)

Annex I: List of EMEP-stations.

COUNTRY	Station code ¹⁾ and name	Location lat. long.		Height above sea (m)	Components determined													Operation from ²⁾ to			
					Precipitation						Aerosols					Gases					
					pH	H ⁺	SO ₄	NO ₃	NH ₄	Mg	Na	Cl	Ca	SO _x	TSP	H ⁺	NO ₃	NH ₃	SO ₂	NO ₂	
Austria	A2 Illmitz	47°46'N	16°46'E	117	x	x	x	x	x									x	1 Jan 1978		
Belgium	B1 Offagne	49°53'N	5°12'E	420	x		x	x	x									x	1 Aug 1978		
Czechoslovakia	CS1 Svratouch	49°44'N	16°02'E	737	x		x											x	1 Oct 1977		
	CS2 Chopok	48°56'N	19°35'E	2008	x		x											x	1 Jan 1978		
Denmark	DK1 Færøerne	62°18'N	7°04'W	210	x	x	x	x	x										1 Feb 1978	16 Oct 1978	
	DK3 Tange	56°21'N	9°36'E	13	x		x	x	x							x	x		10 Jan 1978		
	DK5 Keldsnor	54°44'N	10°44'E	9	x		x	x	x							x	x		1 Jan 1978		
	DK7 Færøerne-Akraberg	61°24'N	6°40'W	90	x		x	x	x							x	x		1 Nov 1978		
Finland	SF4 Ahtäri	62°33'N	24°13'E	162	x	x	x	x	x									x	1 Oct 1977		
	SF6 Kõskar	59°55'N	20°55'E	10	x	x	x											x	6 Oct 1977	30 Sep 1979	
	SF7 Virolahti	60°31'N	27°41'E	8	x	x	x	x	x									x	1 Oct 1977		
	SF9 Utö	59°47'N	21°23'E	7	x	x	x	x	x									x	16 Jan 1980		
France	F1 Vert-le-Petit	48°32'N	2°22'E	64	x	x	x	x	x									x	1 Jan 1978		
	F3 La Crouzille	46°00'N	1°22'E	460	x	x	x	x	x									x	1 Jan 1978		
	F5 La Hague	49°37'N	1°50'W	133	x	x	x	x	x									x	1 Jan 1978		
	F6 Valduc	47°35'N	4°52'E	470	x	x	x	x	x									x	1 Jan 1978		
	F7 Lodeve	43°42'N	3°20'E	252	x	x	x	x	x									x	1 Jan 1978		
German Democratic Republic	DD1 Arkona	54°41'N	13°26'E	42														x	1 Jan 1981		
	DD2 Neuglobsow	53°09'N	13°02'E	62	x		x	x	x									x	1 Jan 1981		
	DD3 Wahnsdorf	51°07'N	13°41'E	246																	
Germany Federal Republic of	D1 Westerland	54°55'N	8°18'E	12	x	x	x											x	x	1 Oct 1977	
	D2 Langenbrügge	52°48'N	10°45'E	74	x	x	x											x	x	1 Oct 1977	
	D3 Schauinsland	47°55'N	7°54'E	1205	x	x	x											x	x	1 Oct 1977	
	D4 Deuselbach	49°46'N	7°03'E	480	x	x	x											x	x	1 Oct 1977	
	D5 Brotjackirriegel	48°49'N	13°13'E	1016	x	x	x											x	x	1 Oct 1977	
	D11 Hohenwestedt	54°06'N	9°40'E	75														x	x	1 Oct 1977	
	D12 Bassum	52°51'N	8°43'E	52														x		1 Oct 1977	
	D13 Rodenberg	52°19'N	9°22'E	148														x		1 Oct 1977	
	D14 Meinerzhagen	51°07'N	7°38'E	510														x		1 Oct 1977	
	D15 Usingen	50°20'N	8°32'E	485														x		1 Oct 1977	
	D16 Bad Kreuznach	49°50'N	7°52'E	230														x		1 Oct 1977	
	D17 Ansbach	49°18'N	10°34'E	481														x		1 Oct 1977	
D18 Rottenburg	48°29'N	8°56'E	427														x		1 Oct 1977		
D19 Starnberg	48°01'N	11°21'E	729														x		1 Oct 1977		
D20 Hof	50°19'N	11°53'E	568														x		1 Jul 1980		
Greece	GR1 Aliartos	38°13'N	23°00'E	110														x		1 Oct 1977	
Hungary	H1 K-pusztá	46°58'N	19°35'E	125	x	x	x	x	x									x	x	1 Oct 1977	
Iceland	IS1 Rjúpnahed	64°05'N	21°51'W		x		x													1 Sep 1978	27 Dec 1979
	IS2 Irafoss	64°05'N	21°01'W		x		x													8 Jan 1980	
Ireland	IR1 Valentia Observatory	51°56'N	10°15'W	9	x		x													11 Feb 1980	
Netherlands	NL2 Witteveen	52°49'N	6°40'E	18	x	x	x	x	x									x	x	1 Oct 1977	30 Nov 1978
	NL5 Rekken	52°06'N	6°43'E	25	x	x	x	x	x									x	x	3 Aug 1980	
	NL6 Appelscha	52°57'N	6°18'E	10	x	x	x	x	x									x	x	1 Oct 1977	
Norway	N1 Birkenes	58°23'N	8°15'E	190	x		x	x	x											1 Oct 1977	
	N8 Skreådalen	58°49'N	6°43'E	475	x		x	x	x											1 Oct 1977	
	N15 Tustervatn	65°50'N	13°55'E	439	x		x	x	x											1 Oct 1977	
	N30 Jergul	69°24'N	24°36'E	255	x		x	x	x											1 Oct 1977	
	N35 Narbuvoll	62°21'N	11°28'E	768	x		x	x	x											1 Oct 1977	

Annex I: Location of EMEP-stations.





NORSK INSTITUTT FOR LUFTFORSKNING

NILU

(NORGES TEKNISK-NATURVITENSKAPELIGE FORSKNINGSRÅD)
 POSTBOKS 130, 2001 LILLESTRØM
 ELVEGT. 52.

TLF. (02) 71 41 70

RAPPORTTYPE Teknisk Rapport	RAPPORT NR. TR 5/83	ISBN--82-7247-
DATO 20/5-83	ANSV.SIGN. B.Ottar	ANT. SIDER 42
TITTEL Experience and future perspectives of the NMR Expert Group on air pollution measurements 1975-1982.		PROSJEKTLEDER B.Ottar
		NILU PROSJEKT NR. 20275/ 0-8324
FORFATTER(E) B.Ottar		TILGJENGELIGHET** A
		OPPDRAKSGIVERS REF.
OPPDRAKSGIVER Nordisk Ministerråds sekretariat i Oslo		
3 STIKKORD (å maks. 20 anslag) luftforurensninger	Norden	metoder
REFERAT (maks. 300 anslag, 5-10 linjer)		
TITLE		
ABSTRACT (max. 300 characters, 5-10 lines. gives a survey of methods for sampling and chemical analysis and for evaluation of air pollution data developed in the Nordic countries with support from the Nordic Ministerial Council during the years 1975-1982 for the purpose of examining the long range transport of air pollutants. It also includes suggestions for future co-operative studies in the Nordic countries.		
BO/ ek 20.mai 1983		

**Kategorier: Åpen - kan bestilles fra NILU A
 Må bestilles gjennom oppdragsgiver B
 Kan ikke utleveres C