MEASUREMENT OF ACID PRECIPITATION IN NORWAY

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ABSTRACT

Since January 1972, chemical analysis of daily precipitation samples from about 20 background stations in Norway has been carried out on a routine basis. Air monitoring is carried out at six stations.

The chemical analysis programme is: sulphate, pH and acidity in precipitation, sulphates and sulphur dioxide in air. In addition, more detailed chemical analysis of aerosol and precipitation has been carried out at selected stations. Some results for the measurement period 1972-1974 are presented. Comparison of air and precipitation concentrations of sulphur compounds show that the precipitation scavenging efficiency is very high under the conditions in Southern Norway.

INTRODUCTION

In connection with the OECD Programme "Long Range Transport of Air Pollutants", a monitoring programme based on daily air and precipitation samples was started in October 1971.

This monitoring network was designed to give quantitative data for the deposition of air pollutants in the exposed parts of Norway where extensive damage to freshwater fish was known to occur. In addition to providing data from representative sites to check and control atmospheric models for transport of air pollutants in the OECD Programme, the network was also designed to measure the actual deposition of the deposition of air pollutants in the part of Southern Norway where extensive damage to freshwater fish was known to occur. Because of the orographic precipitation effects (Nordø, 1972), precipitation sampling was considered most important. Air monitoring was included at some of the sampling sites (Figure 1).

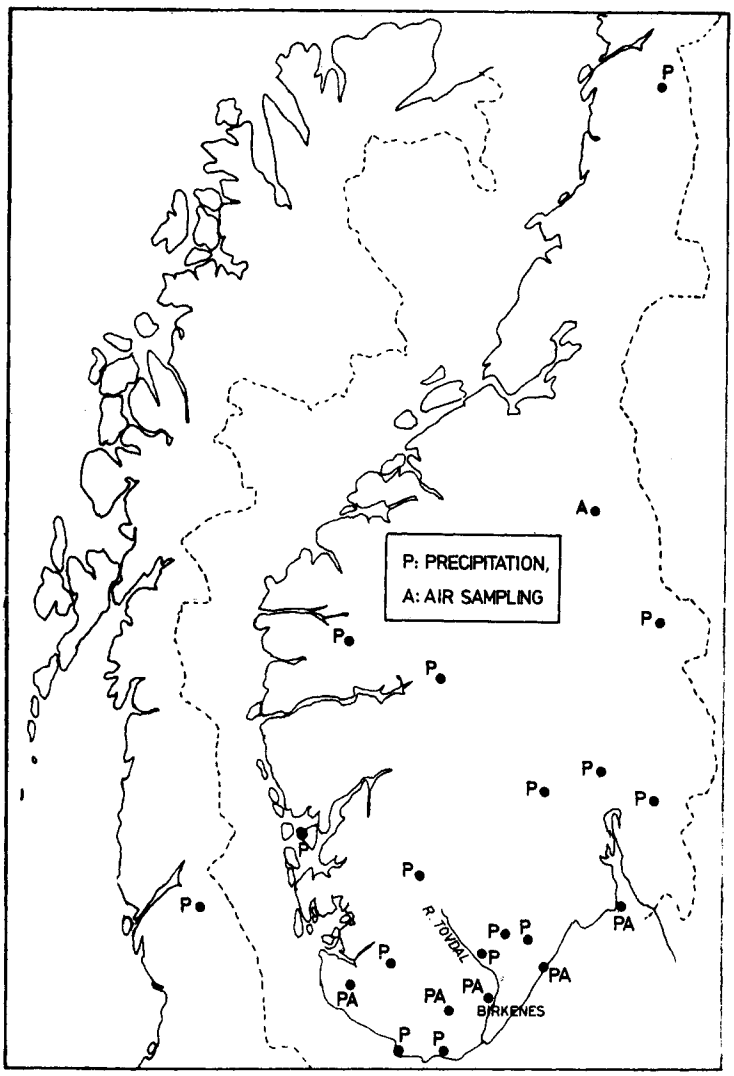

Figure 1. LRTAP Ground Sampling Stations in Norway.

SAMPLING AND ANALYSIS METHODS

The programme included determination of sulphur dioxide as sulphate by the barium-perchlorate-thorin method (Persson, 1966) after absorption in an acid hydrogen peroxide solution, determination of airborne particulate sulphate by X-ray fluorescence (Grennfelt et al., 1971), sulphate in precipitation by the barium-perchlorate-thorin method after ion exchange, and the excess acidity due to strong acids by Gran's plot titration (Liberti et al., 1972).

In addition to this programme, chemical parameters were determined at one of the stations since April 1974. The additional components include nitrate, ammonium, calcium, potassium and sodium in precipitation and aerosol samples, and strong acid in the aerosol samples (Brosset, 1973). Ammonium is determined by the indophenol blue reaction, nitrate by a method based on reduction to nitrite and diazotation (Selmer-Olsen and Henriksen, 1970), while the additional components are determined by standard laboratory methods.

Air monitoring was carried out with simple air pollution sampling equipment (OECD, 1964). Precipitation gauges from polyethylene were used for precipitation sampling. The gauges were made to WMO specifications. Open, dustfall-type polyethylene jars are used for snow collection. The gauges are rinsed with distilled water every day at the time of sample collection.

In the selection of sampling sites WMO criteria for regional background stations were followed (WMO, 1971). Special care was taken to avoid influence of local sources, and the stations were generally placed sites in elevated, or hilly country. Stations in the meteorological precipitation network were generally preferred.

Because of the orographic effects, the amount of precipitation is very variable from one place to another, as illustrated in Figure 2. Also the amount of precipitation varies from one year to another. Compilation of the precipitation chemistry data has shown, however, that the mean weighted concentration of sulphate is a more conservative parameter (Figures 3-5). It is seen that there is a marked gradient from the coast to the inland, and that the pattern of the mean weighted concentrations is consistent from one measurement period to another. Some additional precipitation data from the SNSF-project is included in Figure 5.

From the precipitation data and the data in Figures 3-5, the yearly precipitation amount of sulphate may be calculated. In the maximum zone the deposition of sulphate by precipitation is up to about 5 g SO_4/m^2 year. The emission of sulphur dioxide from sources in the Oslofjord area are about half of the total emission in Norway. The contribution from the local sources in this area is estimated to be 10-30%, and is probably reflected in the precipitation data for 1972 (Figure 3).

Most of the wet deposition due to long range transport takes place in a few events with heavy precipitation. Table I gives a listing of individual days accounting for 50% of a yearly deposition of sulphate. Such events may be critical for small water systems.

The air concentrations of sulphur dioxide and sulphate are generally low and the frequency distributions of sulphur dioxide and sulphate are approximately lognormal (Figure 6).

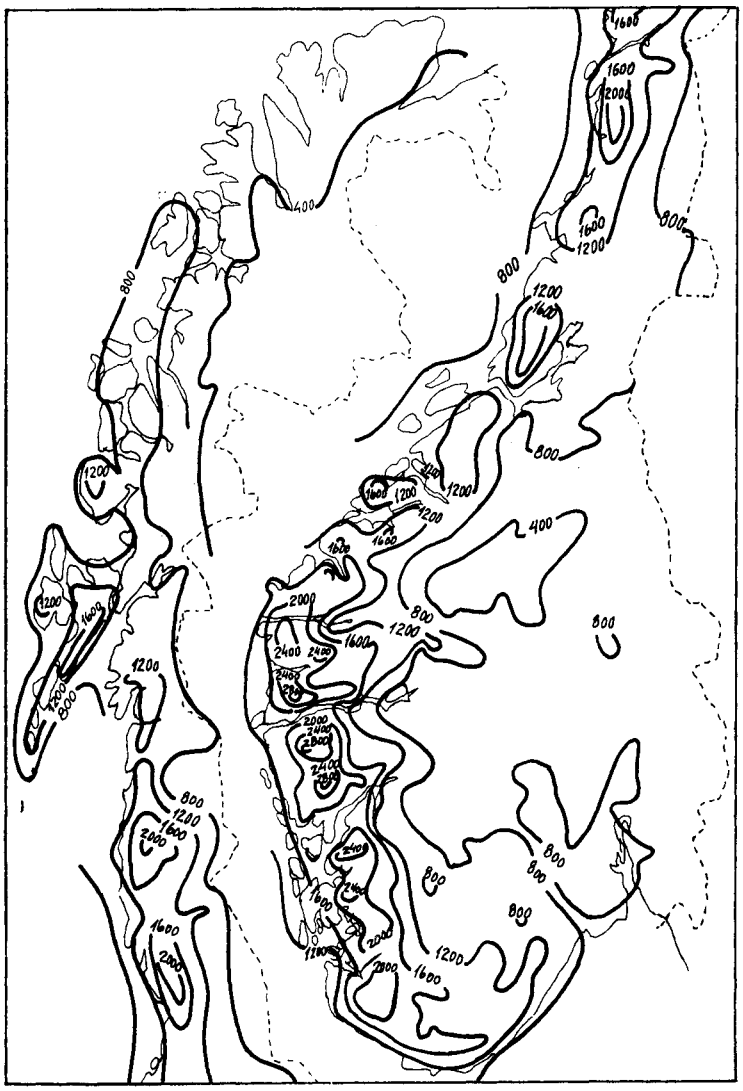

Figure 2. Mean yearly precipitation (mm) in Norway 1901-1930. After I Bruun (1949).

The detection limit for the sulphur dioxide method is about 3 $\mu g/m^3$, and a more sensitive method is desirable for the measurement of sulphur dioxide on a day-to-day basis.

The measured air concentrations are, however, consistent with trajectory calculations based on standard values for the rate of SO_2 removal by dry deposition and transformation from SO_2 to sulphates (Eliassen and Saltbones, 1975). Applying standard values for the dry deposition velocity of SO_2, this deposition may be roughly estimated from the ambient air concentrations to around 50% of the sulphate

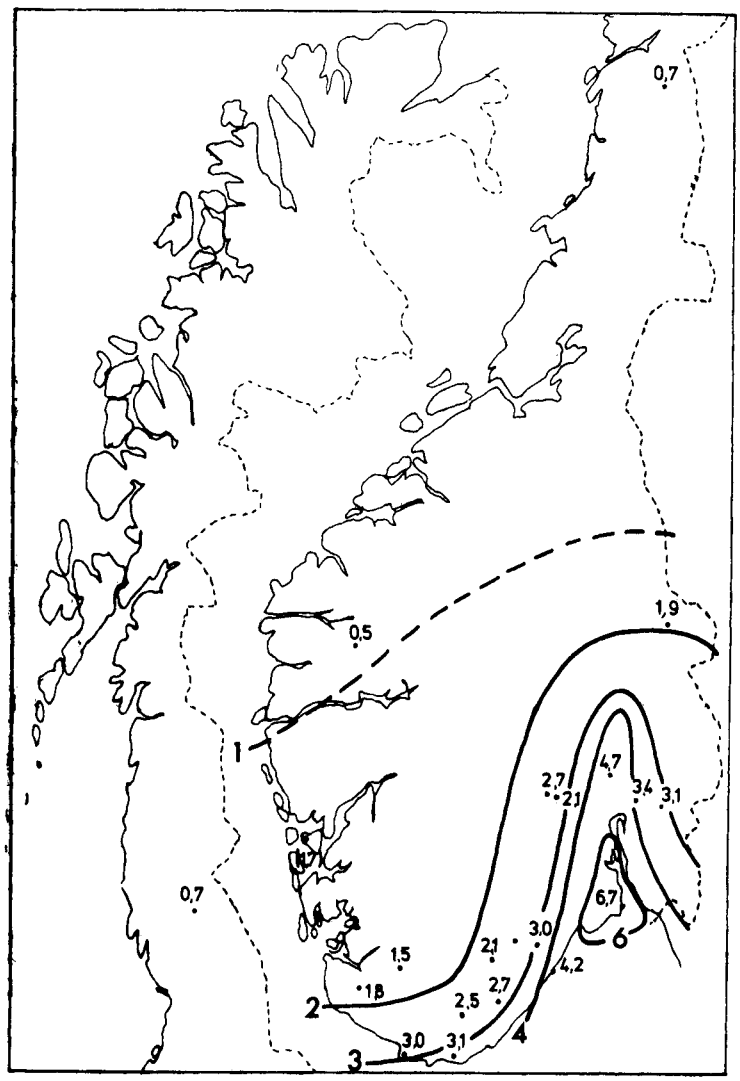

Figure 3. Mean weighted concentrations of sulphate in precipitation. July - December 1972. Unit: mg SO_4/ℓ.

deposition by precipitation.

Aerosol sulphate is generally associated with ammonium, but there is sometimes a considerable proportion of ammonium hydrogen sulphate or sulphuric acid aerosol. Ammonium and sulphate usually makes up 30-50% of the aerosol mass. In precipitation nitrate is also an important constituent, and the acidity is generally well described by the sum of nitrate and sulphate equivalents minus ammonium. Weighted mean concentrations in precipitation for one year is given in Table I, and mean concentrations of watersoluble precipitation and aerosol

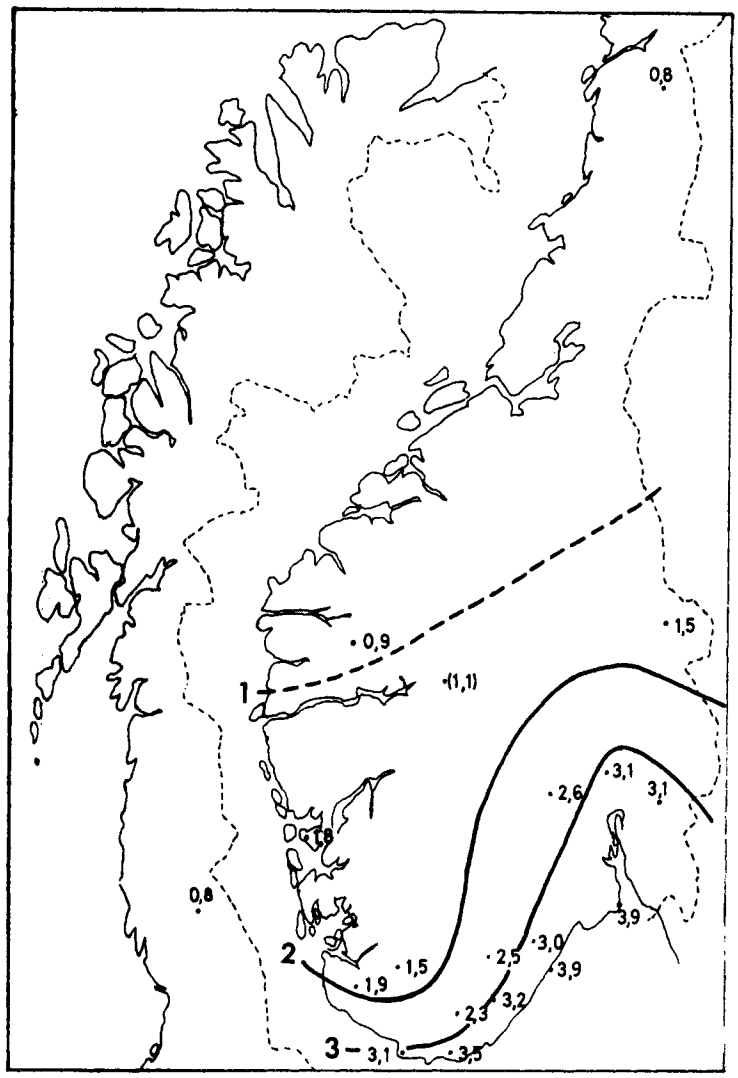

Figure 4. Mean weighted concentrations of sulphate in precipitation. January - December 1973. Unit: mg SO_4/ℓ.

constituents for a three-month period in 1973 are given in Figure 7. An episode with highly acid aerosol was observed in the period 23rd to 31st May 1973, concurrently with similar observations in Sweden (Brosset et al., 1975).

One of the objectives of the precipitation network is to provide input data for effect studies. An example of the impact of precipitation on freshwater chemistry is given in Table II, which summarizes calculated deposition and runoff in one of the rivers in Southern

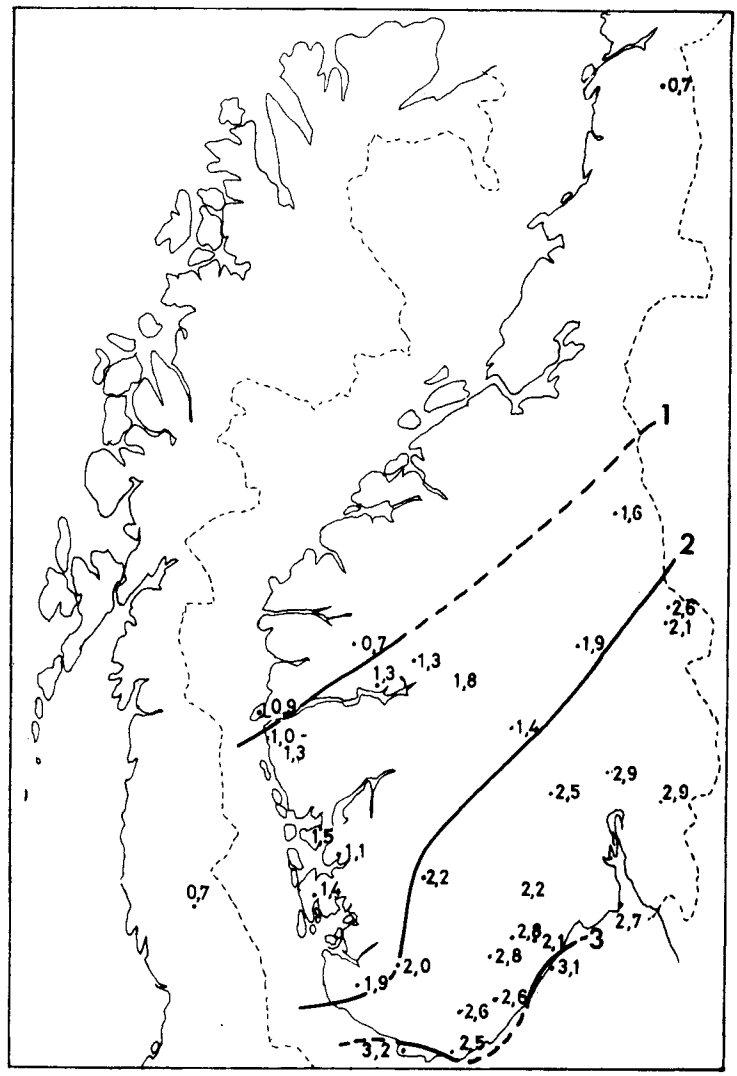

Figure 5. Mean weighted concentrations of sulphate in precipitation. July - September 1974. Unit: mg SO_4/ℓ.

Norway for 3 hydrological years. Both nitrate and ammonium concentrations in the river water are much lower than in precipitation, presumably because of biological fixation. Sulphate is therefore the main anion species in the river water and the runoff can be estimated by the runoff of hydrogen ions and total hardness. It is seen from the table that this runoff corresponds well with the sulphate precipitation. The 20% excess runoff can readily be explained as due to dry deposition and precipitation collection efficiency.

Table I.

Major precipitation events and weighted mean concentrations in precipitation at Birkenes in 1974.

Date	Precip. mm	H^+ µeq/l	NH_4-N mg/l	Ca mg/l	NO_3-N mg/l	SO_4 mg/l	SO_4 mg/m^2	% of total
741019	68,1	113	0,95	0,17	0,91	5,0	339	6,53
741018	36,6	42	0,21	0,09	0,20	4,6	169	8,55
741124	34,7	105	0,92	0,21	0,89	4,8	167	11,77
740107	29,8	91	1,61	0,40	1,30	5,6	166	14,99
741119	15,3	239	0,20	0,06	0,38	10,8	164	18,15
740902	37,4	50	0,63	0,43	0,41	3,9	147	20,98
740916	21,5	107	1,00	0,43	0,88	6,8	146	23,79
740108	29,0	96	0,86	0,08	0,58	4,7	136	26,41
740303	13,1	109	2,35	0,88	1,80	9,2	120	28,72
740205	30,9	74	0,60	0,14	0,74	3,4	106	30,76
741108	15,3	123	1,55	0,21	1,30	6,5	100	32,69
740113	35,3	55	0,49	0,14	0,47	2,8	100	34,62
740826	6,6	152	-	1,27	-	15,3	98	36,51
740109	13,4	84	2,10	0,45	1,19	7,2	96	38,36
740110	22,0	29	1,00	1,06	1,15	4,1	91	40,11
740302	8,3	110	2,50	1,98	2,30	11,0	91	41,86
741114	39,6	47	0,46	0,17	0,35	2,2	88	43,56
740907	46,2	31	0,25	0,17	0,23	1,9	87	45,24
740111	30,2	14	0,71	0,09	0,35	2,8	85	46,88
740216	8,1	248	1,00	0,22	1,45	10,2	83	48,48

Mean weighted concentrations

	H^+	NH_4-N	Ca	NO_3-N	SO_4
mg/l	-	0,52	0,21	0,50	3,24
µeq/l	59	37	11	35	69

Total precipitation (1974): 1562,7 mm

The sulphate concentrations in the 155 lakes sampled in connection with the SNSF regional lake survey also reflect the main structure of the precipitation sulphate concentrations in Figures 3-5

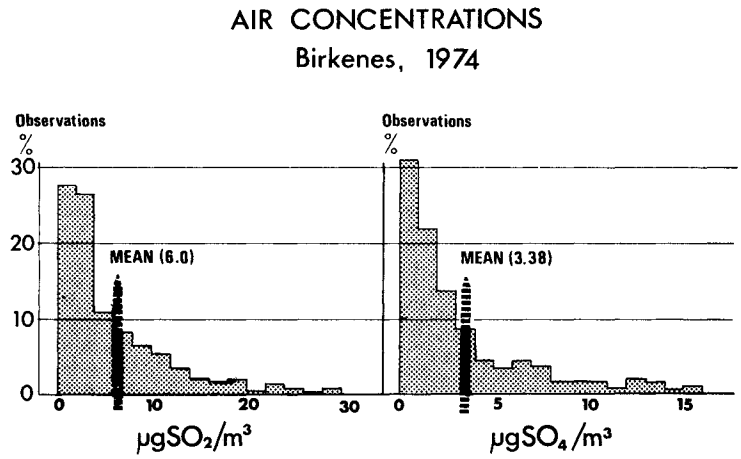

Figure 6. Frequency distribution of daily mean concentrations of sulphur dioxide and sulphate in air. Birkenes 1974.

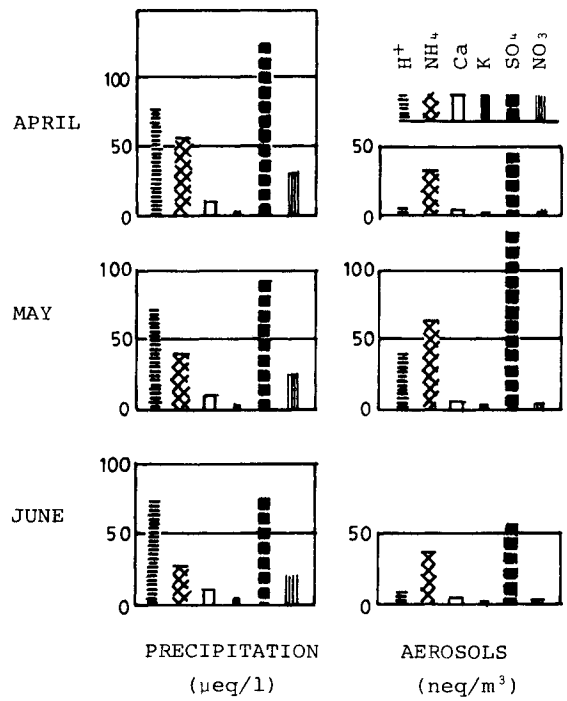

Figure 7. Mean concentrations of watersoluble constituents in air and precipitation at Birkenes in southern Norway. May - June 1973.

Table II.

Precipitation and deposition of sulphate with precipitation in the River Tovdal watershed, compared with river runoff for 3 hydrological years, September 1971 - August 1974.

PRECIPITATION		RUNOFF			
Water ($m^3 \times 10^{-6}$)	SO_4^{--} (equivalents $\times 10^{-6}$)	Water ($m^3 \times 10^{-6}$)	H^+ ($eq.10^{-6}$)	ΣMe^+ ($eq.10^{-6}$)	Total ($eq.10^{-6}$)
2083	150	1731	24	174	198
1864	115	1260	17	120	137
1620	112	1221	18	135	153

(Wright et al., 1975). Slightly higher concentrations are found in southeastern parts where evaporation is more important in relation to the annual precipitation. Also the contribution by dry deposition may be more important in this region.

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