A study of the acidity in the precipitation in Southwestern Norway

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(Manuscript received October 23; revised version December 12, 1972)

ABSTRACT

Using 6-hourly samples of precipitation at Lista, the influence of local and remote sources of acid precipitation in Southwestern Norway is discussed. The distribution of pH values for different wind directions indicates that the acidity in this area is hardly caused by local sources. A study of the trajectories of the rainbearing airmasses shows that the highest acidity in Southwestern Norway occurs in airmasses passing over the major industrial areas in Central Europe and the United Kingdom.

1. Introduction

Theoretically, there are various acids that may cause high acidity (low pH values) in precipitation. Junge (1963), however, states that most observations point to sulphuric acid (H_2SO_4) as the important agent for low pH values in rainwater. H_2SO_4 is formed both by natural processes (oxidation of hydrogen sulphide (H_2S) produced in certain sea and land areas, e.g. intertidal flats, marshes, shallow lakes, etc.), and as a result of anthropogenic activity (oxidation of sulphur dioxide (SO_2) from the burning of fossil fuels).

The acidity in the precipitation varies considerably, both in time and in space. Studies of the geographical distribution of acidity in the precipitation over Northern Europe indicate that the yearly acid deposition is increasing, and that there is a relationship between industrial activity and the acidity (Odén, 1968; Sweden's case study for the UN conference on the human environment 1972).

But even non-industrial areas in Southern Norway receive rather acid precipitation. At Lista (58°06′ N, 6°34′ E, see Fig. 4), the median annual pH value for the period 1962–1966 was as low as 4.6 (Persson, 1968). The local emissions of SO_2 in this area was unimportant, and can hardly explain the low pH values observed. It has been assumed that the lifetime of SO_2 in the atmosphere is too short to permit advection of acidifying substances to Southern Norway from Central and Western Europe. Junge (1963) thus suggests that the low pH values along the Norwegian coast cannot be accounted for by artificial SO_2, but may be related to natural production of H_2S in coastal areas or in the sea.

But the relative amounts of anthropogenic SO_2 deposited and remaining airborne depend on many factors. Present estimates of the effective lifetime of SO_2 in the atmosphere range from one hour to several days (Pasquill, 1972). Rodhe (1972) estimated a turnover time of 2–4 days for anthropogenic sulphur over Northern Europe, and his calculations indicated that the sulphur deposition in Southern Sweden is significantly affected by foreign antropogenic sources. Thus it is possible that the acid precipitation in Southwestern Norway has distant as well as local sources.

2. Sampling procedures

Until recently most of the observations of the acidity in the precipitation in Norway were based on monthly samples. This made it difficult to reveal the source(s) of the acids. In the present study precipitation was collected every sixth hour (at 00, 06, 12, and 18 GMT) at Lista lighthouse, a permanent station in the Norwegian meteorological network.

The Lista peninsula (Fig. 3) is a rural district, consisting mainly of cultivated fields, heather moors and some marshes. In the sampling

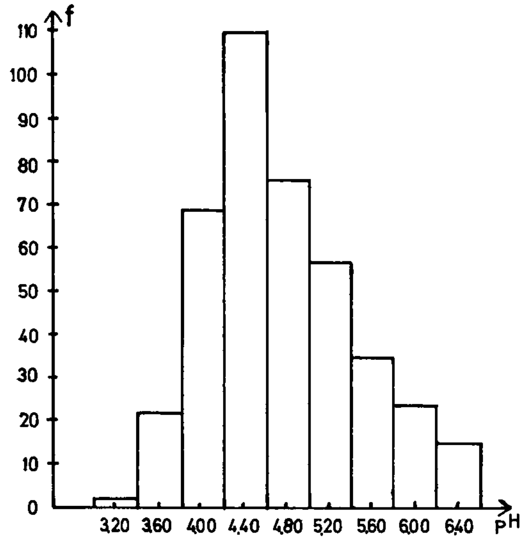

Fig. 1. Frequency distribution of pH values in 410 precipitation samples collected at Lista in the period 10 December 1969 to 1 January 1971.

period there was no large-scale industry in the area.

The precipitation collector was placed about 150 m from the shoreline and about 15 m above sea level. The opening of the collector was about 1.6 m above the ground. The precipitation was collected by a glass funnel (opening diameter 27 cm) leading the water into a 2 l plastic bottle. This bottle was placed in an insulated cabinet; heated in the cold season. The bottles were changed every sixth hour, and were thoroughly cleaned and dried before used again.

Originally the precipitation was stored in glass or plastic bottles until it was analyzed. But it appeared that the pH values often changed considerably during storage. To avoid this uncertainty the pH value was measured immediately after the collection of each precipitation sample.

3. Discussion

410 samples of precipitation were collected at Lista during the period 10.12.1969 to 1.1.1971. Most of the samples were analyzed immediately

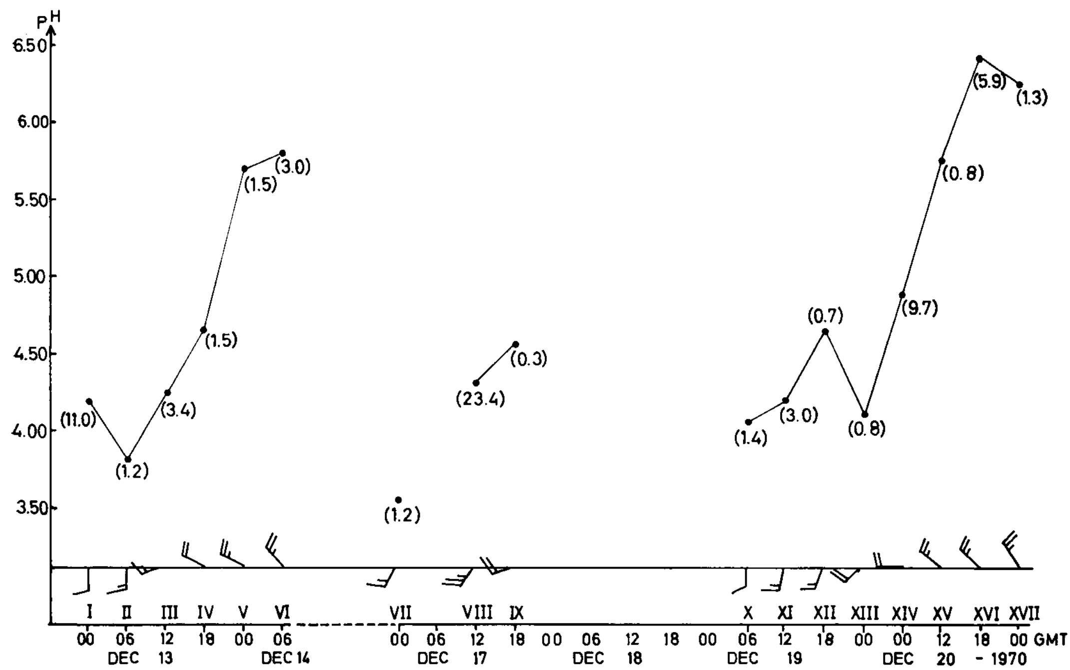

Fig. 2. pH values in precipitation collected at Lista in the period 13 December to 20 December 1970. The values in brackets are precipitation amounts (mm). 6-hourly averages of the wind direction and speed observed at Lista are indicated at the bottom of the figure. The Roman numerals give the correspondence with the trajectories of the rainbearing airmasses shown in fig. 4.

after collection. The frequency distribution of the pH values is shown in Fig. 1. The highest pH value observed was 6.58 (14.12. 1970 at 18 GMT) while the lowest was 3.09 (29.12.1969 at 00 GMT). The average pH value ($\overline{pH} = 1/N\sum pH_i$) was 4.73, and the median pH value was 4.63. (For comparison of different methods of calculating average pH values, see e.g. Odén (1968). In the present study the difference between the $\overline{pH}$ values and the median values was generally less than 0.1 pH units.)

Fig. 2 shows the variations of the pH value at Lista for the period 13.12.1970 to 20.12.1970. There are rather large fluctuations in the pH value from term to term. A general decrease in the acidity with time is indicated in the two periods with successive precipitation terms. This trend may be a result of rainout/washout processes. But the pH value apparently also depends on the local wind direction. If it, as a first hypothesis, is assumed that the acidity in the precipitation at Lista merely is influenced by local sources, the interrelation between the pH value and the local wind direction may be used to identify these sources.

A) *Local influences on the acidity in the precipitation at Lista*

The most probable explanations of local acidification at Lista may be divided into two categories:

I. *Acid contribution from sources on land:*

(*a*) Oxidation of SO_2 formed by burning of fossil fuels at Lista.

(*b*) Oxidation of H_2S formed by reduction of sulphate in marshes, shallow lakes or the soil.

(*c*) Supplies of other acids (HNO_3, HCl, etc.) with local sources.

II: *Acid contribution from sources at sea or at the waterside:*

(*d*). Oxidation of H_2S formed in intertidal flats.

(*e*) Acid contribution from the sea (see e.g. (Barrett & Brodin, 1955).

In case acid precipitation is formed merely by either (*a*), (*b*) or (*c*), the lowest pH values should be expected when the winds are blowing from land; while the explanations (*d*) and (*e*) ought to give lowest pH values for winds blowing from the waterside. To examine this, the 6-hour average wind direction ($\overline{dd}$) was calculated from the synoptical observations of the wind direction (dd) at Lista. The average wind direction was characterized as "undetermined" for 6-hour periods with calm, and in periods with changing wind direction ($|dd - \overline{dd}| > 030°$).

Table 1 gives the relationship between the average wind direction ($\overline{dd}$) and the acidity. The values in brackets are frequencies estimated from the hypothesis H_{01}: "The pH value in the precipitation at Lista is independent of the wind direction". The estimated frequencies (e_{ij}) are calculated from (1) $e_{ij} = n_{i\cdot}\, n_{\cdot j}/n$, where $n_{i\cdot}$ and $n_{\cdot j}$ are sums of frequencies in the ith row and jth column respectively. n is total number of frequencies.

Table 1 shows that there is good accordance between observed and estimated frequencies when the wind blows from N and NE. Winds from SE and S, however bring more precipita-

Table 1. *pH values in precipitation at Lista for winds from different sectors*

Average wind direction (°)	Observed and estimated[a] frequencies $3.0 \leq pH < 4.2$	$4.2 \leq pH < 5.4$	$5.4 \leq pH < 6.6$	$n_{i\cdot}$	Precipitation amount (mm)	Average pH value $\overline{pH}$	S.D. S_{pH}
N 330–020	2 (2)[a]	4 (5)	3 (2)	9	12.6	4.92	0.69
NE 030–080	2 (3)	10 (10)	4 (3)	16	169.0	4.89	0.74
SE 090–140	44 (28)	74 (72)	7 (25)	125	932.1	4.40	0.53
S 150–200	12 (7)	22 (20)	0 (7)	34	285.6	4.38	0.42
SW 210–260	7 (11)	38 (29)	5 (10)	50	308.9	4.79	0.54
NW 270–320	1 (17)	31 (44)	44 (15)	76	446.9	5.48	0.52
$n_{\cdot j}$	68	179	63	$n = 310$			
"Undetermined" wind direction				100	785.3	4.62	0.65
Total				410	2 940.4	4.73	0.69

[a] The values in brackets are frequencies estimated from (1) $e_{ij} = (n_{i\cdot}\, n_{\cdot j}/n)$.

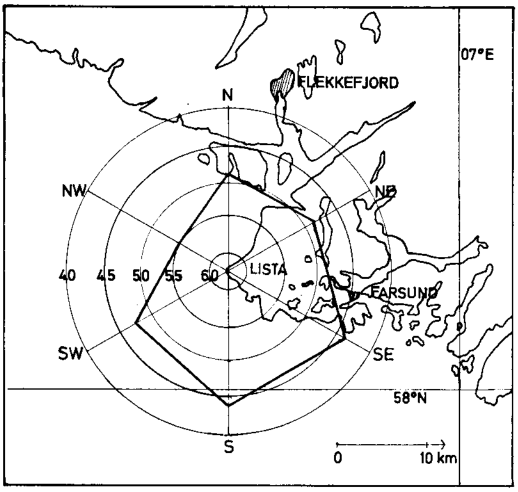

Fig. 3. Average pH values in precipitation at Lista for winds from different sectors.

tion samples with "very low pH value" (pH < 4.20) and fewer with "high pH value" (pH ⩾ 5.40) than expected from H_{01}. For winds from SW there are fewer samples with pH < 4.20 and pH ⩾ 5.40 than estimated from H_{01}. Winds from NW give many more samples with "high pH value" than one should expect if the pH value was independent of the wind direction. Application of the χ^2-test shows that the hypothesis H_{01} must be rejected. In the present case one can conclude that the pH value in the precipitation at Lista is significantly dependent on the wind direction.

Fig. 3 shows the average pH value for six wind direction sectors. It appears that the precipitation is most acid ($\overline{\text{pH}} \sim 4.4$) for winds from SE and S, while winds from NW bring the least acid precipitation ($\overline{\text{pH}} \sim 5.5$) to Lista. For winds from N and SE the pH value may be influenced by the minor SO_2 emissions from the two small towns Flekkefjord and Farsund (each with a population of about 8 000). But an interesting feature is that there is no marked distinction in the $\overline{\text{pH}}$ values for winds from the waterside and winds from land. The precipitation is just as acid for winds from SE (land) as for winds from S (waterside). Similarly, the acidity is virtually the same either the winds blow from N (waterside) or from NE (land).

Consequently, the acid precipitation at Lista can hardly be explained by merely one of the processes (*a*)–(*e*). It remains a possibility of local acidification by a combination of processes from the two categories. In that case the distribution of $\overline{\text{pH}}$ values at Fig. 3 must be interpreted as if the acid contribution from process (*a*)–(*c*) in sector SE is just as important as the contribution from (*d*)–(*e*) in sector S. But this explanation is very unlikely. The topographical conditions at the waterside are rather uniform in the three "sea sectors" S, SW and NW. Accordingly one should expect the same acid contribution from each of these sectors. Fig. 3 shows, however, that this is not the case; the $\overline{\text{pH}}$ value varies significantly between these three sectors.

These features indicate that local sources hardly can be the main contributors to the acid precipitation at Lista. The variation in the pH values with the local wind direction is probably due to a link between the wind direction and the trajectories of the rainbearing airmasses.

B) *Distant influences on the acidity in the precipitation at Lista*

Most of the large industrial and urban areas in Northern Europe are situated at a distance of about 500–1 000 km from Lista; i.e. in the area between the two circles drawn in Fig. 4. From this zone, the "source zone", any potential acidifying substances must be brought to Lista through a "transport zone" (the inner circle; radius 500 km). Perhaps with the exception of sector NE–SE, the anthropogenic SO_2 emissions in the transport zone are unimportant (cf. Sweden's case study, 1971).

To study the acidity in airmasses with different "source areas", trajectories were constructed for airparcels arriving at Lista in the middle of a 6-hour term with precipitation. Rodhe (1972) suggests that the height to be chosen for calculation of trajectories in connection with studies of sulphur transport over long distances, should be around 1 km, if only one height is used. The trajectories in this study are based on the geostrophic wind (see e.g. Durst et al., 1959) at the surface level, and may thus be supposed to give a useful approximation to geostrophic trajectories just above the friction layer (cf. Godske et al., 1957, p. 767), i.e. at a height of about 1 km.

Trajectories for airmasses giving precipitation at Lista in the period 13.12 to 20.12.1970 are shown in Fig. 4. The figure suggests a relation-

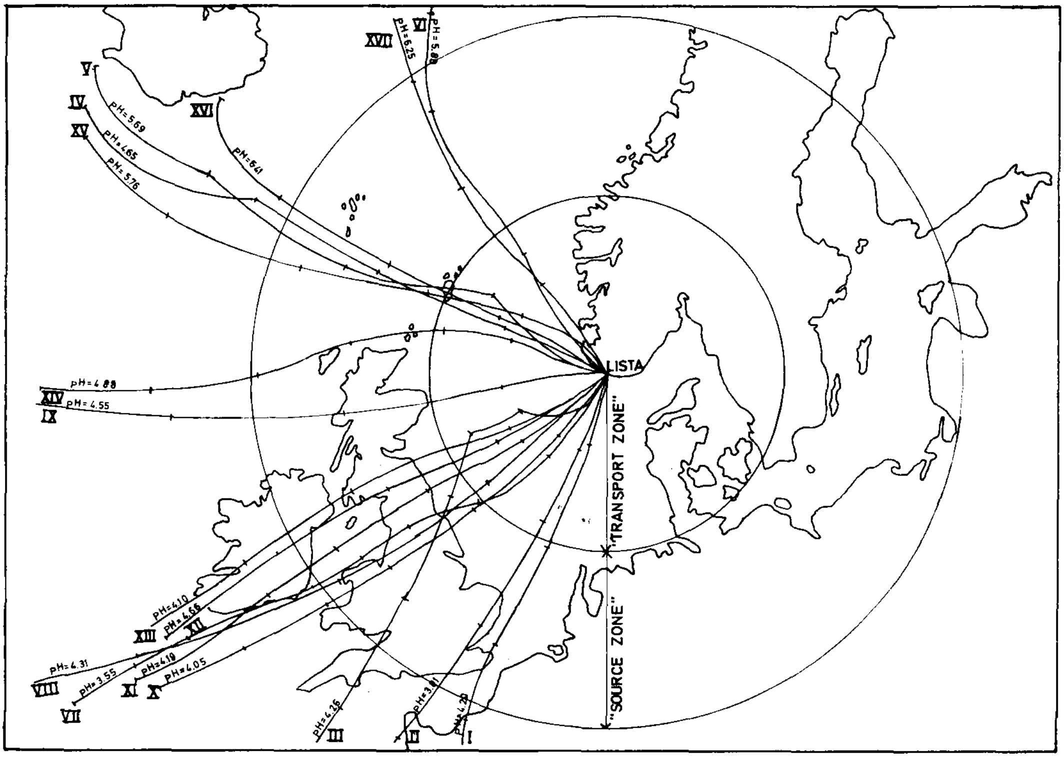

Fig. 4. Trajectories for airmasses giving precipitation at Lista in the period 13 December to 20 December 1970. The trajectories are marked with Roman numerals, corresponding to the marking of the individual precipitation samples in Fig. 2. The crosslines indicate the positions of the individual airparcels for every sixth hour.

ship between the trajectories of the rainbearing airmasses and the pH value. Precipitation from airmasses passing over the industrial areas in the United Kingdom is apparently more acid than that from airmasses coming from the Norwegian Sea.

Geostrophic trajectories may, however, deviate significantly from the "true" trajectories of the airparcels (see e.g. Danielsen, 1961); thus one should be very careful in drawing conclusions from individual trajectories. To reduce this uncertainty, all trajectories were grouped according to their direction and curvature in the source zone and the transport zone. For a group consisting of several cases, the average pH value is believed to be fairly representative for that category of trajectories.

Average pH values and typical trajectories (TR) for airparcels having approximately straight tracks are shown in Fig. 5 (solid lines). Table 2 gives more detailed information about these trajectories. The values in brackets are frequencies expected according to the hypothesis H_{02}: "The pH value in the precipitation at Lista is independent of the trajectories of the rainbearing airmasses." Table 2 shows that for TR = 3B, 4A, 4B, 5A and 5B there are more samples than expected from H_{02} having a "very low pH value" (pH <4.20) and fewer than expected having a "high pH value" (pH $\geqslant 5.40$). About 60% of the samples with TR = 4A and 4B (airmasses from Western Germany, the BeNeLux-countries and Northern France) have a pH <4.20, while merely 4% have a pH $\geqslant 5.40$.

For TR = 6B, 7A, 7B and 8A (airmasses from the Atlantic and the Norwegian Sea) there are, according to H_{02}, a deficiency of samples with pH <4.20 and an excess of samples with pH $\geqslant$ 5.40. For TR = 6B (the Atlantic) merely 2% of the samples have a pH <4.20. For TR = 7A and

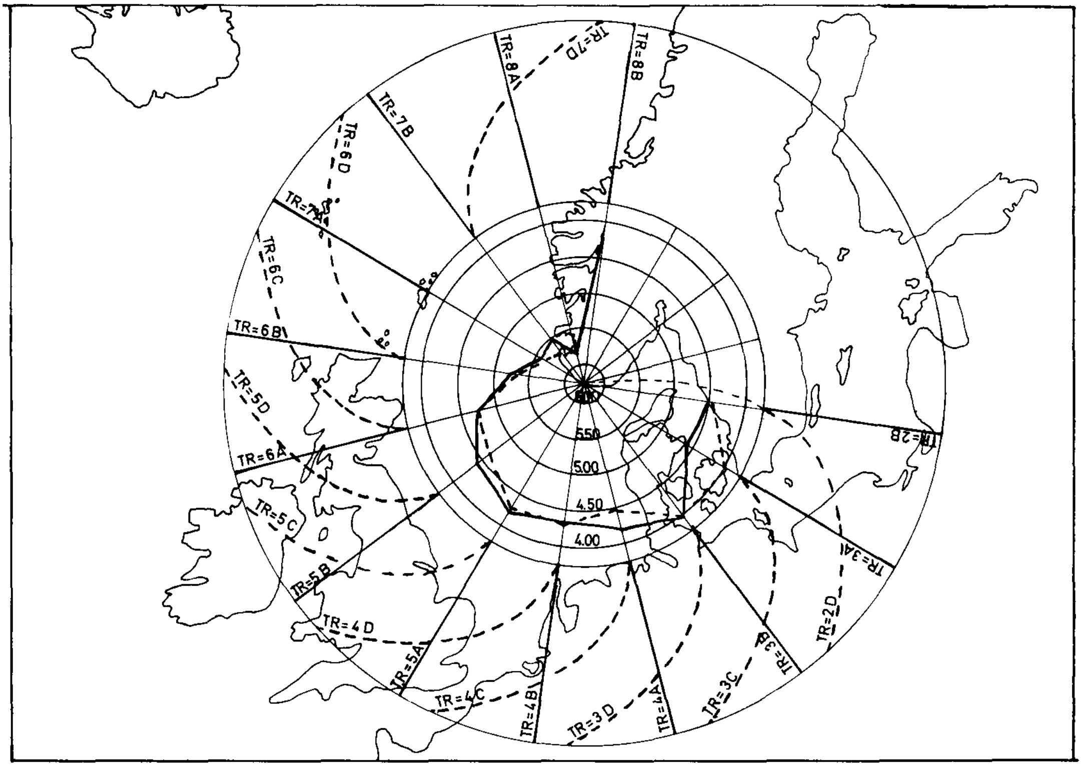

Fig. 5. Average pH values in precipitation at Lista for airmasses with approximately straight trajectories (solid lines) and for airmasses with "moderate" cyclonic curved trajectories (broken lines). Each of the trajectories shown represent trajectories within a sector of approximately $\pm 11°$.

Table 2. *pH values in precipitation at Lista for airmasses with approximately straight trajectories*

Trajectory-direction TR "Source area"	Observed and estimated[a] frequencies $3.0 \leq pH < 4.2$	$4.2 \leq pH < 5.4$	$5.4 \leq pH < 6.6$	$n_{i.}$	Precipitation amount (mm)	Average pH value ($\overline{pH}$)	S.D. (S_{pH})
2B The Baltic	0 (0)[a]	2 (1)	0 (0)	2	9.0	4.50	0.19
3A Poland	0 (1)	3 (2)	0 (1)	3	3.6	4.58	0.15
3B E. Germany	6 (2)	4 (6)	0 (2)	10	52.9	3.96	0.38
4A W. Germany	9 (3)	3 (7)	1 (3)	13	32.9	4.18	0.44
4B BeNeLux, N. France	7 (3)	7 (8)	0 (3)	14	87.4	4.34	0.32
5A S. England	8 (5)	15 (13)	0 (5)	23	276.5	4.22	0.37
5B Wales, N. England	12 (8)	25 (23)	2 (8)	39	383.7	4.43	0.52
6A N. Ireland, S. Scotland	5 (9)	37 (25)	1 (9)	43	304.0	4.73	0.36
6B The Atlantic, N. Scotland	1 (12)	38 (34)	20 (13)	59	432.9	5.27	0.52
7A The Norwegian Sea	1 (4)	3 (13)	18 (5)	22	76.7	5.57	0.57
7B The Norwegian Sea	1 (3)	6 (8)	7 (3)	14	53.1	5.51	0.67
8A The Norwegian Sea	0 (1)	0 (2)	3 (1)	3	8.2	5.83	0.07
8B The Norwegian Sea, W. Norway	1 (0)	0 (1)	0 (0)	1	2.9	4.00	—
$n_{.j}$	51	143	52	$n = 246$			

[a] The values in brackets are frequencies estimated from (1) $e_{ij} = (n_{i.} n_{.j}/n)$.

Table 3. *Average pH values in precipitation at Lista for airmasses with "moderate" cyclonic curved trajectories*

Trajectory direction		Precipitation amount (mm)	No. of samples	Average pH value ($\overline{pH}$)	S.D. (S_{pH})
TR	"Source area"				
2D	Poland, S. Sweden	7.7	2	4.45	0.00
3C	E. Germany	0.9	1	4.00	—
3D	W. Germany	10.0	3	3.98	0.57
4C	BeNeLux, W. Germany	125.1	8	4.47	0.44
4D	S. England	300.3	18	4.32	0.45
5C	N. Ireland, Central England	90.1	13	4.29	0.46
5D	N. England	106.3	10	4.64	0.37
6C	Norwegian Sea, Scotland	54.3	9	4.74	0.45
6D	Norwegian Sea	9.9	2	5.31	0.19
7D	Norwegian Sea	16.4	1	5.73	—

7B (the Norwegian Sea) merely 6% of the samples have a pH < 4.20, while about 70% have a pH ≥ 5.40. For TR = 6A (airmasses from Northern Ireland and Southern Scotland) there is a deficiency of both "high" and "very low" pH values, while as much as 86% of the samples have pH values in the interval 4.20 ≤ pH < 5.40.

Compared to H_{02}, airmasses passing over the highly industrialized areas in Northern Europe (TR = 3B, 4A, 4B, 5A and 5B) seem to give an excess of precipitation samples with "very low" pH values, while airmasses coming from sea areas (TR = 6B, 7A, 7B and 8A) seem to give an excess of samples with "high" pH values. Application of the χ^2-test shows that this tendency is significant.

Fig. 5 shows that the lowest average pH value ($\overline{pH}$ = 3.96) occurred for airmasses passing over Eastern Germany and Denmark (TR = 3B), while airmasses from the Norwegian Sea (TR = 8A) gave the highest $\overline{pH}$ value ($\overline{pH}$ = 5.83). Airmasses passing over Central Europe or England (TR = 3B, 4A, 4B, 5A or 5B) are associated with $\overline{pH}$ values in the interval 3.96 – 4.43. The $\overline{pH}$ values for TR = 8B (the Norwegian Sea and Western Norway) and TR = 2B (Russia, the Baltic and Southern Sweden) are rather uncertain, as they are based on only 1 and 2 situations respectively.

It is interesting to compare the $\overline{pH}$ values for trajectories passing over densely and sparsely populated areas. Fig. 5 shows that the $\overline{pH}$ value increases from 4.2 – 4.4 for airmasses passing over the major industrial areas in England, to 4.7 for trajectories over Southern Scotland, to 5.3 for trajectories from the Atlantic via Northern Scotland, and to 5.5 – 5.8 for airmasses from the Norwegian Sea.

The distribution of $\overline{pH}$ values for airmasses with "moderate" cyclonic curved trajectories (broken lines at Fig. 5) are much the same as for the straight trajectories. This is confirmed by Table 3, showing that airmasses passing over Central Europe or England (TR = 3C, 3D, 4C, 4D or 5C) have $\overline{pH}$ values in the interval 3.98–4.47. The most acid precipitation ($\overline{pH}$ ~ 4.0) occurred for airmasses passing over Western Germany (TR = 3D) and Eastern Germany (TR = 3C). The highest pH value (pH = 5.7) occurred in an airmass coming from the Norwegian Sea.

The $\overline{pH}$ value increases from 4.3 for airmasses passing over the industrial areas in England, to 4.6–4.7 for trajectories over Northern England and Scotland, and to 5.3–5.7 for airmasses coming from the Norwegian Sea. These features are also very similar to those of the straight trajectories.

Three more main classes were included (cf. Table 4). Since they comprised rather few cases (7, 12 and 11 respectively), they will not be discussed in detail. 67 precipitation events with uncertain trajectories were not included in the classification.

Table 4 gives a brief summary of the results for the five main trajectory classes. It shows that precipitation from airmasses passing over the industrial areas in Central Europe or England has an average pH value in the interval 4.0–5.0, whereas airmasses arriving at Lista from the Norwegian Sea bring precipitation with $\overline{pH}$ values in the interval 5.1–6.6.

Table 4. *Average pH values in precipitation at Lista for airmasses with different trajectory curvature*

Curvature in					
Source zone	Straight	Moderate cyclonic	Moderate anticycl.	Strongly cyclonic	Moderate cyclonic
Transport zone	Straight	Moderate cyclonic	Moderate anticycl.	Moderate cyclonic	Strongly cyclonic
"Source area"					
Central Europe, England	$4.0 \leqslant \overline{pH} \leqslant 4.4$	$4.0 \leqslant \overline{pH} \leqslant 4.6$	$4.4 \leqslant \overline{pH} \leqslant 4.8$	$4.0 \leqslant \overline{pH} \leqslant 4.4$	$4.3 \leqslant \overline{pH} \leqslant 5.0$
Norwegian Sea	$5.5 \leqslant \overline{pH} \leqslant 5.8$	$5.3 \leqslant \overline{pH} \leqslant 5.7$	$5.7 \leqslant \overline{pH} \leqslant 6.6$	$5.1 \leqslant \overline{pH} \leqslant 5.6$	$5.1 \leqslant \overline{pH} \leqslant 5.9$

4. Concluding remarks

The present study shows that the pH value in the precipitation at Lista varies considerably with the time. For the period 10.12.1969 to 1.1.1971 the highest and lowest pH values observed at Lista for 6-hourly terms were 6.58 and 3.09 respectively. The median pH value for this period was as low as 4.63.

The soil in Southwestern Norway has little ability to neutralize the acid precipitation. As a result salmon fishes already have vanished from some rivers and lakes in this area. In the future the acid precipitation may have serious consequences for the agriculture and the forestry (cf. Sweden's case study, 1971).

Both the distribution of the average pH values for different wind directions and the relationship between the trajectories of the rain-bearing airmasses and the $\overline{pH}$ values strongly suggest that the acids in the precipitation at Lista must have remote sources. Thus the average pH values lie in the interval 4.0–5.0 for airmasses from Central Europe or England, while airmasses from the Norwegian Sea are associated with $\overline{pH}$ values in the interval 5.1–6.6. Evidently one can conclude that the acid precipitation in Southwestern Norway mainly is a result of the SO_2 emissions in the major industrial countries in Northern Europe.

5. Acknowledgements

The author wants to thank Professor Dr K. Utaaker for many valuable suggestions, and Mr I. Dugstad and Mr Y. Gjessing for useful discussions.

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ИЗУЧЕНИЕ КИСЛОТНОСТИ В ОСАДКАХ В ЮГО-ЗАПАДНОЙ НОРВЕГИИ

На основе 6-часовых проб осадков в Листа обсуждается влияние локальных и удаленных источников кислотности осадков в юго-западной Норвегии. Распределение величин pH для различных направлений ветра указывает, что кислотность в этой области едва ли вызывается местными источниками. Изучение траекторий воздушных масс, несущих осадки, показывает, что наибольшая кислотность в юго-западной Норвегии наблюдается для воздушных масс, прошедших над основными индустриальными областями Центральной Европы и над Великобританией.